Transactions of the Materials Research Society of Japan 28 [1] 157-160 (2003)

Characterization of PLZT Thick Film Prepared by MOCVD

Yoshihisa.Honda, Shintaro.Yokoyama and Hiroshi.Funakubo
Department of Innovative and Engineered Materials, Tokyo Institute of Technology,
4259 Nagatsuta-cho, Midori-ku , Yokohama, 226-8502, Japan
Fax: 81-45-924-5446, e-mail: honda@iem.titech.ac.jp

Epitaxial $(Pb_{1-x},La_x)(Zr_{0.3},Ti_{0.7})O_3$(PLZT) films were grown by metalorganic chemical vapor deposition (MOCVD) on (100)MgO substrates from $Pb(C_{11}H_{19}O_2)_2$ - $La(C_{14}H_{25}O_2)_3$ - $Zr(O\cdot t\text{-}C_4H_9)_4$ - $Ti(O\cdot i\text{-}C_3H_7)_4$ - O_2 system. The La/(Pb+La) ratio of the film linearly increased while the Zr/(Zr+Ti) ratio kept constant when the input flow rate of La source gas increased under the constant gas flow rates of other metal sources. This suggests the good composition controllability of MOCVD-PLZT film compatible to PZT film in spite of the fact that PLZT film consisted of as much as four elements. (100)- and (001)-oriented PLZT films having the Zr/(Zr+Ti) ratio of 30% were epitaxially grown on (100)MgO substrates up to the La/(Pb+La) ratio of 33%. The lattice parameter ratio of *c*- to *a*-axis, tetragonallity, of these films decreased with increasing the La/(Pb+La) ratio and transformed to cubic phase when the La/(Pb+La) ratio was 18%. Crystal-orientation-perfection of these films drastically increased by the La substitution when the La/(Pb+La) ratio was only 1% and was almost constant from 7 to 18% but contrary decreased at 33%. Film thickness linearly increased up to 4μm with increasing the deposition time while the film composition was maintained. On the other hand, the crystal orientation perfection increased with increasing the film thickness. This shows that the good quality-epitaxial thick PLZT films up to 4μm in thickness were ascertained to be grown by MOCVD with high reproducibity.
Key words; PLZT, MOCVD, thick film

1. INTRODUCTION

PLZT material has been known to have high electro-optic coefficient in sintered body and is already applied for various applications such as optical shutter [1]. Thick film of PLZT has been attractive for device in view of the integration and the cost. PLZT thick films have been prepared by several preparation methods, such as pulse d -laser deposition (PLD) [2], sol-gel method [3] and metalorganic chemical vapor deposition (MOCVD) [4-5]. Among these techniques, MOCVD is recognized as the most important preparation methods from a practical point of view because of its good step-coverage which is effective for preparing three dimensional waveguide and of its ability to prepare high-quality film with high deposition rate. However, the report of MOCVD-PLZT thick films has been limited. This is because of the difficulty of the control of the film composition, which strongly affect the film property. In the present study, we used a novel La source and grown epitaxial PLZT films on (100)MgO substrates. Controllability of the film composition, and the crystal structure changes with the film composition and the film thickness were investigated.

2. EXPERIMENTAL

PLZT films were prepared on (100)MgO substrates at 650°C by MOCVD using a cold-wall type reactor from $Pb(C_{11}H_{19}O_2)_2$ - $La(C_{14}H_{25}O_2)_3$ - $Zr(O\cdot t\text{-}C_4H_9)_4$ - $Ti(O\cdot i\text{-}C_3H_7)_4$ - O_2 system. $La(C_{14}H_{25}O_2)_3$ [Asahi Denka Kogyo K.K.] kept at 178°C was used as a novel liquid source, in which the melting temperature was 50°C. Only the input source gas flow rate of La source, $R[La(C_{14}H_{25}O_2)_3]$, was changed under the constant input gas flow rates of Pb, Zr and Ti sources; $R[Pb(C_{11}H_{19}O_2)_2]$=5.0mol·cm^2/min, $R[Zr(O\cdot t\text{-}C_4H_9)_4]$=3.5mol·cm^2/min and $R[Ti(O\cdot i\text{-}C_3H_7)_4]$=8.2mol·cm^2/min. Here, the theoretical input gas flow rate of each source gas flow rate was defined as *R*[source] [6]. Film thickness was controlled by changing the deposition time.

Crystal structure and the film orientation were characterized by X-ray diffraction (XRD, Philips X'Pert-MRD). The perfection of the crystal orientation was estimated by the full width at half maximum (*FWHM*) and the peak intensity of the rocking curve of the PLZT *002*. The film composition, film thickness, and the deposition rates of each constituent oxide were estimated by X-ray fluorescence (XRF, Philips PW2404) calibrated by using standard samples. The microstructure of the film and film thickness were investigated by scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

3.1 Composition control of the film

Figure 1 shows the deposition rates of the constituent oxides of the films as a function of $R[La(C_{14}H_{35}O_2)_3]$ under the constant gas flow rates of other sources. Deposition rates of PbO and $LaO_{1.5}$ linearly decreased and increased as shown in Figs.1 (a) and (b), respectively when $R[La(C_{14}H_{35}O_2)_3]$ increased. It must be pointed out that the discontinuous was observed in PbO as shown in Fig.1 (a) when $R[La(C_{14}H_{35}O_2)_3]$ was

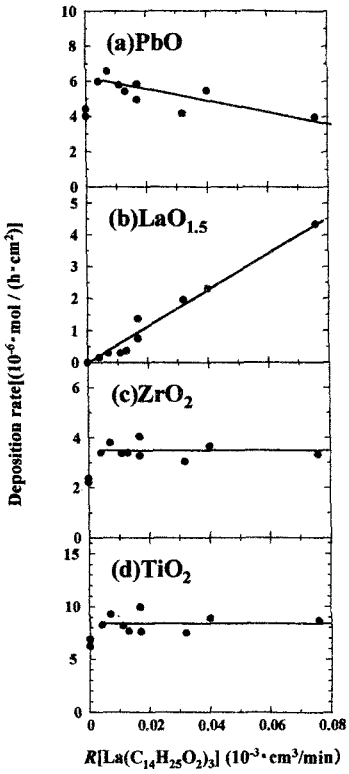

Fig.1 Deposition rates of the constituent oxides of the films as a function of $R[La(C_{14}H_{35}O_2)_3]$ under the constant gas flow rates of other sources (a)PbO (b)$LaO_{1.5}$ (c)ZrO_2 (d)TiO_2.

introduced into the source system. On the other hand, the deposition rate of ZrO_2 and TiO_2 were not almost changed as shown in Fig.1 (c) and (d).

Figure 2 replots the data shown in Fig.1 as a film composition. Taking account of the fact that the combination of Pb and La, and that of Zr and Ti preferentially occupied the A and B sites in perovskite ABO_3, respectively, the ratio of (Pb+La)/(Pb+La+Zr+Ti) shown in Fig.2(c) correspond to the site ratio of the A/(A+B) in the film, while the La/(Pb+La) and the Zr/(Zr+Ti) ratios correspond to La and Zr fraction in A and B sites, respectively. The La/(Pb+La) ratio linearly increased with increasing $R[La(C_{14}H_{35}O_2)_3]$ as shown in Fig.2(a), which reflect the linear decrease and increase of PbO and $LaO_{1.5}$, as shown in Figs.1(a) and (b), respectively. On the other hand, the Zr/(Zr+Ti) and (Pb+La)/(Pb+La+Zr+Ti) ratios were almost constant. This suggests only the La/(Pb+La) ratio in A site linearly increased with $R[La(C_{14}H_{35}O_2)_3]$, keeping constant Zr/(Zr+Ti) ratio and the site ratio of A/(A+B). It means that the deposition rates of PbO and $LaO_{1.5}$ in PLZT consisting of four metal elements are not independent parameter, so that the individual parameter to control the composition was almost the same as PZT consisting of three metal elements. This reveals that the high reproducible preparation of PLZT film was achieved.

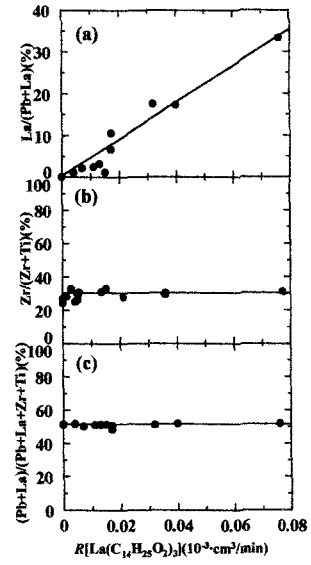

Fig.2 (a)La/(Pb+La), (b)Zr/(Zr+Ti), and (c)(Pb+La)/(Pb+La+Zr+Ti) of the films as a function of $R[La(C_{14}H_{35}O_2)_3]$ under the constant gas flow rates of other sources.

3.2 La/(Pb+La) ratio dependency

Figure 3 shows the change in the XRD patterns with the La/(Pb+La) ratio in the film having the Zr/(Zr+Ti) ratio of 30%. Only tetragonal PLZT *h00* and *00l* were observed regardless of the La/(Pb+La) ratio. These films were confirmed to be epitaxially grown by X-ray pole figure measurement; (100)(001)PLZT//(100)MgO. PLZT *h00* peaks disappeared above the La/(Pb+La) ratio of 18%, suggesting the possibility of the perfectly (001) oriented tetragonal or cubic films.

Figure 4 shows the *a*- and *c*-axes lattice

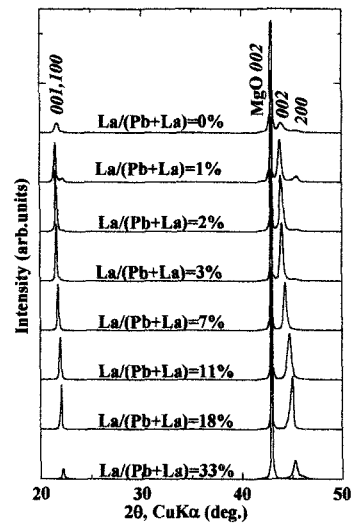

Fig.3 Change in the XRD patterns with the La/(Pb+La) ratio in the film having the Zr/(Zr+Ti) ratio of 30%

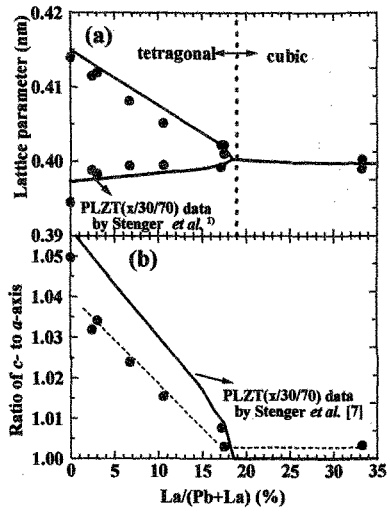

Fig.4 Dependency of (a) a- and c-axes lattice parameters and (b) the c/a lattice parameter ratio on the La/(Pb+La) ratio of the film

parameters and the lattice parameter ratio of c- to a-axis, c/a ratio, of the films as function of the La/(Pb+La) ratio of the same films shown in Fig.3. Solid line in Fig.4 shows the reported data for PLZT powder having the Zr/(Zr+Ti) ratio of 30% by Stenger *et al.* [7]. Lattice parameters of c- and a-axes decreased and increased, respectively, with the increase of the La/(Pb+La) ratio in the film together with the decrease of the c/a ratio. The phase transformation from tetragonal to cubic phase was ascertained when the La/(Pb+La) ratio was 18% by X-ray reciprocal space mapping. However, absolute values of the lattice parameters of c- and a-axes of the films were smaller and larger than those of PLZT powder, respectively together with the small c/a ratio. This is due to the strain effect from the substrate as already pointed out [8].

Figure 5 shows the *FWHM* and the peak intensity of the rocking curve of the PLZT *002* peak for the same films as shown in Figs. 3 and 4. These data can be divided into 4 regions as shown in Fig.5. The *FWHM* and the peak intensity dramatically decreased by the La substitution when the La/(Pb+La) ratio was only 1% as shown in region (I) in Fig.5. This is considered to the increase of the crystal orientation perfection by the decrease of the defects, such as Pb and O, in the film due to the substitution of higher valency La to Pb sites. The peaks intensity increased while the *FWHM* was not changed in the La/(Pb+La) ratio from 1 to 7% as shown in region (II) in Fig.5. This responds to the increase of the crystallinity by the decrease of the c/a ratio in the film as shown in Fig.4 (b). The *FWHM* and the peak intensity were almost constant in the La/(Pb+La) ratio from 7 to 18% as shown in region (III) in Fig.5. This shows the almost crystal-orientation-perfection due to the almost same c/a ratio. Finally the *FWHM* and the peak

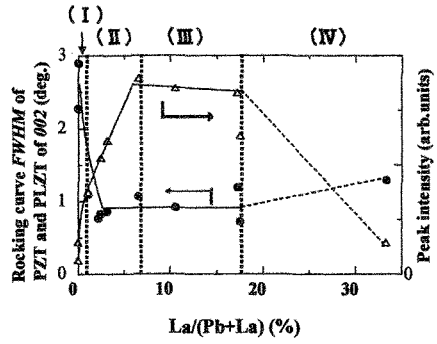

Fig.5 *FWHM* and the peak intensity of the rocking curve of the PLZT *002* peak as a function of the La/(Pb+La) ratio in the film.

intensity increased and decreased, respectively, when the La/(Pb+La) ratio was 33% in region (IV) in Fig.5. This can be explained by the stress unreleased character of the cubic phase without the phase transition, stress release process, during the cooling process [8]. Another possibility is the B site occupancy of the excess La [1]. Detailed analysis is under investigation.

3.3 Film thickness dependency

Figure 6 shows the change of the film thickness with the deposition time for PZT and PLZT single-phase films. Film composition of PZT and PLZT was ascertained to be almost constant in spite of the deposition time; Zr/(Zr+Ti)=30% for PZT films, La/(Pb+La)=2% and Zr/(Zr+Ti)=30% for PLZT films. Film thickness linearly increased with increasing the deposition time for the same films as shown in Fig.6.

Figure 7 shows the change in the XRD patterns with the deposition time. PZT and PLZT films having (100)- and (001)-orientations were ascertained to be grown without the obvious change of the peak position and the orientation.

Figure 8 shows the *FWHM* of the rocking curve of the *002* peaks as a function of the film thickness. It decreased with increasing the film thickness for both films, suggesting the increase of the perfection of the crystal orientation. The

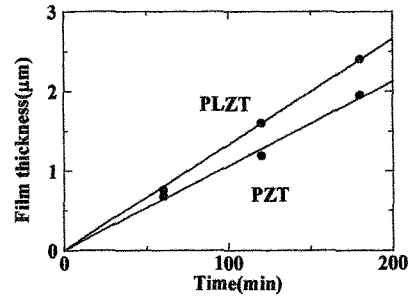

Fig.6 Change of the film thickness with the deposition time for PZT and PLZT films.

strain applied to the film from the substrate is considered to be released when the film thickness increased. Figure 9 shows the cross-sectional SEM image of the PLZT films above 4μm in thickness. Dense film without obvious columnar grain was observed. These microstructures were suitable for the optical application.

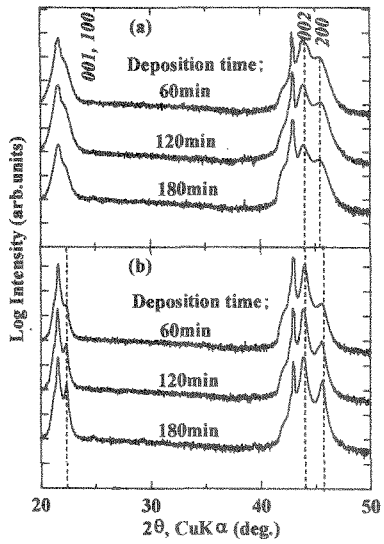

Fig.7 Change in the XRD patterns with the deposition time for (a)PZT and (b)PLZT.

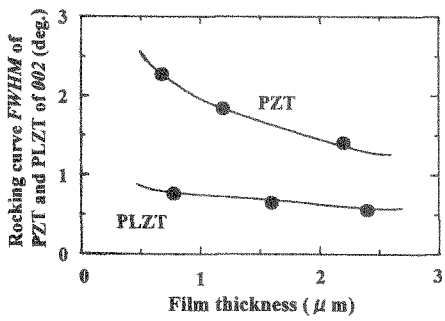

Fig.8 *FWHM* of the rocking curve of the *002* PLZT and PZT peaks as a function of the deposition time

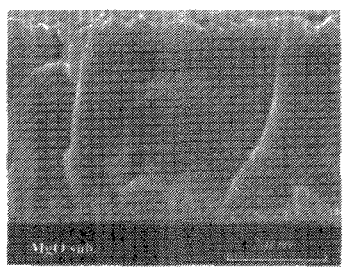

Fig.9 Cross-sectional SEM image of PLZT film grown on (100)MgO substrate La/(Pb+La)=8% Zr/(Zr+Ti)=30%.

CONCLUSION

(100)- and (001)-oriented epitaxial PLZT thick films were grown on (100)MgO substrates by MOCVD. Deposition rates of PbO and $LaO_{1.5}$ in PLZT consisting of four metal elements are not independent parameter, so that the individual parameter to control the composition was almost the same as PZT consisting of three metal elements. This reveals that high reproducible preparation of PLZT film was achieved.

The *FWHM* and the peak intensity dramatically decreased by the La substitution when the La/(Pb+La) ratio was only 1%. The peaks intensity increased while the *FWHM* did not changed in the La/(Pb+La) ratio from 1 to 7%. The *FWHM* and the peaks intensity were almost constant in the La/(Pb+La) ratio from 7 to 18%. The *FWHM* and the peaks intensity increased and decreased, respectively when the La/(Pb+La) ratio was 33%. Dence 4μm thick PLZT film was obtained by increasing the deposition time. Crystal-orientation-perfection increased with the film thickness.

The *FWHM* of the rocking curve of the *002* peaks as a function of the deposition time decreased with increasing the deposition time for both films.

ACKNOLEDGEMENT

The authors would like to thank Asahi Denka Kogyo K.K. for supplying us with $La(C_{14}H_{25}O_2)_3$ material source.

REFERENCES

[1] G. H. Haertling and C. E. Land, *J. Am. Ceram. Soc.*, **54**, 1-11 (1971).
[2] Y.M.Kang, J.K.Ku and S.Baik, *J. Appl. Phys.*, **78**, 2601-2606 (1995).
[3] R.E.Jones, Jr.,P.D.Maniar, J.O.Olowolafe, A.C.Campbell and C.J.Mogab, *Jpn. J. Appl. Phys.*, **60**, 1022-1024 (1992).
[4] M.Shimizu, H.Fujisawa and T.Shiosaki, *Integrated Ferroelectrics*, **10**, 23-30, (1995).
[5] H.Funakubo, K.Imashita and N.Mizutani, *Ceramic letter*,**11**, 1169-1171(1991).
[6] T.Matsuzaki, N.Okuda, K.Shinozaki, N.Mizutani and H.Funakubo, *Jpn. J. Appl. Phys.*, **37** 6229-6232 (1998).
[7] C.Stenger and J.Burggraaf, *J. Phys. Chem. Solids*, **41**, 17-23 (1980).
[8] M.Otsu, H.Funakubo, T.Hioki, K.Shinozaki, T.Akai and N.Mizutani, *Chem. Soc. Jpn.*, **10**, 789-795 (1994).

(Received December 21, 2002; Accepted January 31, 2003)