Characterization of Epitaxially Grown CVD-Pb(Zr, Ti)O₃ Films with High Deposition Rate

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高速でエピタキシャル成長させた CVD-Pb(Zr, Ti)O₃ 薄膜の特徴

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Pb(Zr_xTi_{1-x})O₃ films with good surface flatness were deposited by CVD using the gas mixture of Pb(DPM)₂-Zr(O-*t*-Bu)₄-Ti(O-*i*-Pr)₄-O₂. The epitaxially grown Pb(Zr_xTi_{1-x})O₃ films were deposited on (100)MgO substrates with 300 nm/min of the deposition rate. This deposition rate is the highest among the reported value. The existence of the grains with slight different angle along the film thickness was ascertained by TEM observation. It was attributed to the volume change at the Curie temperature and to the large temperature dependence of *a*- and *c*-axes lattice parameters of Pb(Zr_xTi_{1-x})O₃ film compared with that of MgO substrate below the Curie temperature. The refractive index of this film was in good agreement with that reported for Pb(Zr_xTi_{1-x})O₃ crystal without post heat-treatment and its dispersion can be fitted the Sellmeier dispersion formula.

Key-words: Epitaxial film, Pb(Zr_xTi_{1-x})O₃, CVD, High deposition rate

1. Introduction

The lead zirconate-lead titanate system [Pb(Zr_xTi_{1-x})O₃] is a typical ferroelectric material that shows a high dielectric constant, an electro-optical effect and a spontaneous polarization.¹⁾ Potential applications of this film include pyroelectric detector, surface acoustic device, optical shutter, optical modulator and nonvolatile memories. Thin films with several microns in thickness is necessary for some applications such as pyroelectric detector. Therefore the preparation method with high deposition rate, more than several ten nanometers per minutes, is desirable for the practical point of view.

Pb(Zr_xTi_{1-x})O₃ thin film has been prepared by practical methods,^{2),3)} such as vacuum method and sputtering. CVD is one of the most effective method for the preparation of this film because it is characterized by the high controllability of the composition and crystal structure, and good step coverage. Until

now, several papers have been appeared describing the growth of Pb(Zr_xTi_{1-x})O₃ films by CVD. We have already reported the preparation of tetragonal Pb(Zr_xTi_{1-x})O₃ films by CVD from Pb(C₁₁H₁₉O₂)₂, Zr(O-*t*-C₄H₉)₄, Ti(O-*i*-C₃H₇)₄, and O₂ as starting materials.⁴⁾ Almost epitaxially grown Pb(Zr_xTi_{1-x})O₃ films with 300 nm/min of the deposition rate were prepared on (100)MgO substrates. In the present paper, we characterize the Pb(Zr_xTi_{1-x})O₃ film with high deposition rate.

2. Experimental

In the preparation of Pb(Zr_xTi_{1-x})O₃ film by CVD, the selection of starting material is a substantial point. In the present study, we selected Pb(C₁₁H₁₉O₂)₂ [Pb(DPM)₂] as a starting material of lead. This compound melts about 132°C but is stable up to 280°C without decomposition. Therefore, we can control the Pb(DPM)₂ vapor pressure steadily and precisely not from the solid but from the liquid for wide temperature range. Moreover, this compound is proved not to be toxic, while Pb(C₂H₅)₄ and Pb(C₃H₇)₄ which are widely used for the preparation of Pb(Zr, Ti)O₃ film, are toxic. We previously reported the first paper for the use of this compound as a source material of lead.⁴⁾ As starting materials of Zr and Ti, we selected Zr(O-*t*-C₄H₉)₄ [Zr(O-*t*-Bu)₄] and Ti(O-*i*-C₃H₇)₄ [Ti(O-*i*-Pr)₄], respectively. These are liquid at room temperature and have high vapor pressure near the room temperature to be able to control their vapor pressures by blowing the carrier gases into them.

The CVD apparatus used in the present study was almost the same as that for the preparation of (Pb, La)(Zr, Ti)O₃ film,⁵⁾ and BaTiO₃ and SrTiO₃ films.⁶⁾ Ti(O-*i*-Pr)₄ and Zr(O-*t*-Bu)₄ vapors were generated by bubbling N₂ gas into each liquid, and Pb(DPM)₂ vapor was generated by heating its powders and carried by N₂ gas. The vapor pressures of Ti(O-*i*-Pr)₄ and Zr(O-*t*-Bu)₄ could be controlled by its temperature and the flow rate of carrier gas. On the other hand, that of Pb(DPM)₂ could be controlled by only its heating temperature.

These vapors were mixed with preheated O₂ and

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Table 1. Deposition Conditions of Epitaxially Grown Pb(Zr_xTi_{1-x})O₃ Film

Precursor	Pb : Pb(DPM) ₂ Zr : Zr(O·t-Bu) ₄ Ti : Ti(O·i-Pr) ₄
Temperature of vaporizer	Pb : 135 - 140 °C Zr : 40 - 50 °C Ti : 30 - 40 °C
Flow rate of carrier for each component	Pb : 180 sccm Zr : 20 - 40 sccm Ti : 20 - 40 sccm
Total gas flow rate	: 480 sccm
Total gas pressure	: 20 Torr
O ₂	: 1.7 Torr (8.3%)
Deposition temperature	: 650 °C
Cooling rate	: 20 °C/min
Substrate	: (100)MgO (10mm x 10mm x 0.5mm)

N₂ gases just before the reaction chamber, and were flowed through a nozzle to a substrate. N₂ gas was a balancing gas to keep total gas flow rate constant. Freshly cleaved (100)MgO single crystal was used as a substrate and was set on the stainless steel block which was heated by an electrical furnace.

O₂ and N₂ gases were dehydrated by P₂O₅ and preheated before introducing into the apparatus. All gas lines were heated about 170°C to prevent the condensation of the source gas. In the present study, we prepared tetragonal Pb(Zr_xTi_{1-x})O₃ film. The deposition conditions of the epitaxially grown Pb(Zr_xTi_{1-x})O₃ films are summarized in Table 1.

The constituent phases and orientation of the film were identified by X-ray powder diffractometer (XRD; Philips, PW-1700). Moreover, the change of XRD pattern with temperature was observed by high-temperature XRD. Microstructure and composition of the films were observed using scanning electron microscopy (SEM; JEOL, JSM-T200) and transmission electron microscopy (TEM; JEOL, TEM-200CX) equipped with EDS (Philips, PV9900). The X-ray excitation area for EDS measurement in TEM observation was estimated to be about 0.08 μm from the diameter of the contamination. The optical transmittance of Pb(Zr_xTi_{1-x})O₃ film together with (100)MgO substrate was measured as a function of wavelength between 0.2 and 0.8 μm at normal indices to the film plane using dual-beam spectrophotometer.

3. Result and discussion

3.1 Deposition rate

The deposition rate could be controlled from 50 to 300 nm/min by altering the distance between the tip of the gas nozzle and the substrate from 10 to 50 mm. Epitaxially grown Pb(Zr_xTi_{1-x})O₃ films were obtained over the all deposition-rate range in the present study. The remarkable effect of the deposition rate on the crystal structure, microstructure and the optical property was not observed within the limit of the present study. This is attributed the fact that the deposition rate was controlled only by altering the concentration of the vapor of the starting

materials near the substrate under the fixed deposition temperature, total gas pressure and the total gas flow rate.

Except the report of the very high deposition rate of the film prepared by electron beam deposition,⁷⁾ the deposition rate in the present study was higher than other reported value of Pb(Zr_xTi_{1-x})O₃ film.⁸⁾⁻¹⁰⁾ Moreover, for the epitaxially grown film, it is about 10 times as fast as that of RF magnetron sputtering¹¹⁾ and is the highest among the all reported value. Okada et al.¹²⁾ reported that the deposition rate of highly *c*-axis oriented Pb(Zr_xTi_{1-x})O₃ film prepared by CVD was 50–100 nm/min. However, the highest deposition rate in the present study was about three times as fast as that of Okada et al.¹²⁾ They used Zr(DPM)₄ as starting materials of Zr, and Zr(DPM)₄ have lower vapor pressure compared with any starting materials used in the present study. Therefore, the selection of the starting material in the present study is more effective for the high speed deposition. Moreover, high total gas pressure condition in the present study (20 Torr) is also effective for the high speed deposition. In the following section, we characterize the film deposited with 300 nm/min of the deposition rate.

3.2 Crystal structure

Figure 1 shows (a) TEM of Pb(Zr_xTi_{1-x})O₃ film

Fig. 1. Bright image and selected area diffractions of Pb(Zr_xTi_{1-x})O₃ film on (100)MgO substrate.

[Zr/(Zr+Ti)=0.5]

- (a) Bright image of Pb(Zr_xTi_{1-x})O₃ film on (100)MgO substrate,
- (b) Selected area diffraction of Pb(Zr_xTi_{1-x})O₃ film,
- (c) Selected area diffraction of the interface of Pb(Zr_xTi_{1-x})O₃ film and MgO substrate,
- (d) Selected area diffraction of MgO substrate.

and selected area diffractions (SAD) of (b) Pb(Zr_xTi_{1-x})O₃ film, (d) MgO substrate and (c) their interface. Only spots of perovskite Pb(Zr_xTi_{1-x})O₃ were observed and no other spot including hallow was observed in Fig. 1(b). Moreover, SAD of interface shown in Fig. 1(c) was composed of that of Pb(Zr_xTi_{1-x})O₃ film and MgO substrate as shown in Figs. 1(b)–(d). Therefore, no interface compound between Pb(Zr_xTi_{1-x})O₃ film and MgO substrate was observed. These results showed that no other phase, including amorphous which could not be detected by XRD, was exist in the film and the interface between the film and the substrate, even though the deposition rate of this film was 300 nm/min. Moreover, the homogeneity of the composition was ascertained by EDS analysis.

Pb(Zr_xTi_{1-x})O₃ film was ascertained to be grown with the same direction as MgO substrate by comparing SAD patterns of Figs. 1(b) and (d). Therefore, Pb(Zr_xTi_{1-x})O₃ film was revealed to be epitaxially grown on MgO substrate. However, each spot in SAD of Pb(Zr_xTi_{1-x})O₃ film was found to be slightly split as shown in Fig. 1(b). This showed that perfect epitaxial growth did not achieved in this film. Sakashita et al.^{13),14)} also reported the splits of the spot in SAD of Pb(Zr_xTi_{1-x})O₃ film with 0.48 and 0.32 of x prepared by CVD with 8–12 nm/min of the deposition rate. The split observed in the present study was among those of 0.32 and 0.48 of x in the report by Sakashita et al. This result shows that the quality of the high speed deposited film in the present study is almost the same as that of Sakashita et al. deposited with 8–12 nm/min. Moreover, taking into account of the data reported by Sakashita et al. the split of each spot increased with the decrease of x in Pb(Zr_xTi_{1-x})O₃.

Figure 2 shows the temperature dependence of the lattice parameters of deposited Pb(Zr_xTi_{1-x})O₃ film. The a - and c -axes lattice parameters of tetragonal phase tend to be equal with the increase of the temperature and transformed into cubic one. This result indicates that Pb(Zr_xTi_{1-x})O₃ film

Fig. 2. Lattice parameter change as a function of temperature. (○, ●) Zr/(Zr+Ti)=0.14, (□, ■) Zr/(Zr+Ti)=0.45, (○, □) heating, (●, ■) cooling.

deposited on (100)MgO substrate at 650°C had cubic symmetry and transformed to the tetragonal during the cooling. As shown in Fig. 2, the transformation from cubic to tetragonal was accompanied by the volume change, and the a - and c -axes lattice parameters change with temperature was larger than that of MgO substrate below the Curie temperature. These are thought to be the reason that the orientation of each grain was slightly different as shown in Fig. 1(b). Moreover, these change increased with the decrease of x in Pb(Zr_xTi_{1-x})O₃ as shown in Fig. 2. Therefore, the split of the spots in SAD is thought to increase with decrease x in Pb(Zr_xTi_{1-x})O₃.

3.3 Microstructure

Figure 3 shows micrographs of the surface and fractured surface of Pb(Zr_xTi_{1-x})O₃ film deposited on (100)MgO substrate with 300 nm/min of deposition rate. It was dense and made up of the particles grown normal to the substrate with almost the same particle size. The surface of the film was fairly flat, which was also ascertained by the transmittance measurement (see Section 3.4). Obvious dependence of the microstructure of Pb(Zr_xTi_{1-x})O₃ films on Zr/(Zr+Ti) was not observed, although Sakashita et al.¹³⁾ reported the fair dependence of the microstructure on Zr/(Zr+Ti).

3.4 Transmittance of the film

Figure 4 shows the transmittance of the film together with MgO substrate as the same film as Fig. 3. The thickness of Pb(Zr_xTi_{1-x})O₃ film was 1.8 μm. The transmittance was raised from approximately 0.34 μm and showed strong interface oscillation. This oscillation proved to be the good surface flatness of the film surface. Moreover, this absorption edge is almost the same as the reported one for Pb(Zr_xTi_{1-x})O₃ crystal¹⁵⁾ and also that of (Pb, La)

Fig. 3. SEM micrographs of surface and fractured surface of Pb(Zr_xTi_{1-x})O₃ film. [Zr/(Zr+Ti)=0.5] (a) Surface, (b) Fractured surface.

Fig. 4. Transmittance spectra of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ film on (100) MgO substrate and MgO substrate. $[\text{Zr}/(\text{Zr} + \text{Ti}) = 0.4]$ Film thickness : $1.8 \mu\text{m}$.

$(\text{Zr}, \text{Ti})\text{O}_3$ film prepared by CVD.⁶⁾ Moreover, it was irrespective of $\text{Zr}/(\text{Zr} + \text{Ti})$ in $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ film. Sreenivas et al.¹⁰⁾ reported that the shift of absorption edge to the longer wavelength was observed for the film including excess Pb element not included in $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ compound. Therefore the large amount of excess Pb element not included in $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ compound did not exist in this film.

Table 2 shows some reported optical properties of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ film.^{8),9),16)-21)} The transmittance at $0.6 \mu\text{m}$ was about 53% as shown in Fig. 4. Taking into account of the fact that this value in the present study included the transmittance of MgO substrate, the quality of this film was almost the same as that prepared by another techniques even though the film thickness was $1.8 \mu\text{m}$.

The refractive index, n , was calculated from the wavelength spacing between adjacent peaks of the interface oscillations in Fig. 4. Figure 5 shows the wavelength dependence of n of the film. n decreased with the increase of the wavelength, which was typical dispersion curve for $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ crystal. The refractive index was about 2.6 at $0.6 \mu\text{m}$, which agreed with the reported one for the $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ crystal with same composition.¹⁵⁾ As shown in Table 2, post heat-treatment after the deposition is generally necessary for the most of the film except for the film prepared by CVD.²¹⁾ Therefore, the film prepared by CVD had good optical quality without the post heat-treatment. However, the refractive index of CVD film reported by Okada et al.²¹⁾ was smaller than the reported for the $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ crystal with same composition.¹⁵⁾ Therefore, this is the first report for the preparation of the film with the same refractive index as same composition crystal without the post heat-treatment.

The dispersion of n with the wavelength could be fitted by Sellmeier dispersion formula as follows:^{5),22)}

Table 2. Literature Data on Some Optical Properties of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ Film. [] Reference Number

references	methods	substrate	composition [$\text{Zr}/(\text{Zr} + \text{Ti})$]	thickness [μm]
Hamada et al. [8]	RF sputtering	(1102) sapphire	0.62	0.6
Sreenivas et al. [9]	DC magnetron sputtering	fused silica	—	—
Sakai et al. [16]	Sol-gel dip coat.	ITO/ fused silica	0.53	0.5 - 3.0
G. Yi et al. [17]	Sol-gel spin coat.	Al_2O_3 /borosilicate glass	0.44	1.0
Krupanidhi et al. [18]	RF magnetron sputtering	fused silica	0.52	2.0
Okada [19]	RF sputtering	fused silica	0.52	2.2
J. Krempasky et al. [20]	RF magnetron sputtering	sapphire	0.6	1.5 - 1.6
M. Okada et al. [21]	CVD	(100)MgO	0.4	~1.0
This work	CVD	(100)MgO	0.4	1.8

heat treatment	transmittance ($0.6 \mu\text{m}$) [%]	refractive index	absorption edge [μm]	
			before heat treat.	after heat treat.
—	60	2.36 ($0.6328 \mu\text{m}$)	0.295	—
600°C 10h	75	—	0.36-0.38	0.34
600°C 2h	50 (3.0 μm)	2.5 (ave)	—	0.33 (0.5 μm) -0.35 (3.0 μm)
600°C 6h	80	2.6 ($0.6328 \mu\text{m}$)	—	0.43
700°C 5h	95	—	0.43	0.35
600°C 3h <	70	—	0.38	0.35
600°C 40 min	50	2.1 (ca. $0.6 \mu\text{m}$)	0.45	0.35
—	68	2.3-2.4 ($0.633 \mu\text{m}$)	0.33	—
—	53	2.5	0.34	—

Fig. 5. Wavelength dependence of the refractive index of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ film on (100) MgO substrate. $[\text{Zr}/(\text{Zr} + \text{Ti}) = 0.4]$ Film thickness : $1.8 \mu\text{m}$.

$$n^2 - 1 = (S_0 \lambda_0^2) / [1 - (\lambda_0 / \lambda)^2] \quad (1)$$

where λ_0 is an average oscillator position and S_0 is an average oscillator. Figure 6 shows the relation between $1/(n^2 - 1)$ and $1/\lambda^2$ for the same $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ film as the same film as Figs. 3 and 4 together with the reported one for $(\text{Pb}, \text{La})(\text{Zr}, \text{Ti})\text{O}_3$ crystal.¹⁵⁾ This data could fit a straight

Fig. 6. Dependence of $1/(n^2-1)$ on $1/\lambda^2$ replotted using the data in Fig. 5.

PLZT(100x/100y/100z) represents $(\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$.

line as shown in Fig. 6. This showed that this data could fit the Sellmeier dispersion formula. It is known that S_0 , which is calculated from the slope of the straight line in Fig. 6, is less affected by the composition in $(\text{Pb}, \text{La})(\text{Zr}, \text{Ti})\text{O}_3$. On the other hand, λ_0 , which is calculated from the intersect value of $1/\lambda^2$ axis in Fig. 6, increase with increasing $\text{Zr}/(\text{Zr}+\text{Ti})$ and is independent of $\text{La}/(\text{Pb}+\text{La})$ in $(\text{Pb}, \text{La})(\text{Zr}, \text{Ti})\text{O}_3$.¹⁵⁾ The calculated line in Fig. 6 had same slope and was between that of PLZT(8/90/10) and PLZT(10/65/35), where PLZT(100x/100y/100z) represents $(\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$. This result also agree with the reported tendency for $(\text{Pb}, \text{La})(\text{Zr}, \text{Ti})\text{O}_3$ crystal. The values of S_0 and λ_0 were estimated to be $1.04 \times 10^{14} \text{ m}^{-2}$ and $0.219 \mu\text{m}$, respectively. As a result, it can be concluded that the film prepared in the present study had good optical quality even though its deposition rate was 300 nm/min.

4. Conclusion

Epitaxially grown $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ films were deposited on (100)MgO substrates by CVD from $\text{Pb}(\text{DPM})_2$, $\text{Zr}(\text{O} \cdot t\text{-Bu})_4$, $\text{Ti}(\text{O} \cdot i\text{-Pr})_4$ and O_2 as starting materials. The maximum deposition rate was 300 nm/min and is the highest among the reported values. The existence of the grains with slight different angle along the film thickness were ascertained by TEM observation. It was attributed to the volume change at the Curie temperature and to the

large temperature dependence of a - and c -axes lattice parameters of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ film compared with that of MgO substrate below the Curie temperature. The refractive index of the film was in good agreement with that reported for $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ crystal without post heat-treatment. Moreover, the wavelength dependence of the refractive index could be fitted the Sellmeier dispersion formula.

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