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Novel electro-optic properties of epitaxially grown (Pb, La)(Zr, Ti)O_3 (PLZT) thin films derived by advanced sol–gel methods

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Abstract

Advanced sol–gel methods using a secondary solvent addition into (Pb, La)(Zr, Ti)O_3 (PLZT) sol–gel solution and a methanol pre-treatment of sapphire substrates are demonstrated. For the secondary solvent addition, the additive affected the crystallinity and electro-optic (EO) property of PLZT films and only methanol addition can improve them. In addition, the methanol pre-treatment is also appeared to be effective to improve film characteristics.

Through these optimizations, epitaxially grown PLZT thin films on r-cut sapphire are obtained and a high Pockels coefficient which is comparable to those of bulk PLZTs is achieved. It is believed that these PLZT thin films are applicable for integrated EO devices and open the door for the future data communication systems.

Keywords: A. Sol–gel processes; C. Optical properties; D. PLZT; E. Functional applications

1. Introduction

Recently, the amount of data communication has been increasing rapidly and highly integrated electro-optic (EO) devices, i.e. optical routers and optical modulators, are considered to be key technology to establish future data communication systems.

One of the candidate materials that can be used in future EO devices is a lanthanum-modified lead zirconate titanate, (Pb, La)(Zr, Ti)O_3 (PLZT), which is known as a transparent complex oxide with a large EO coefficient [1]. For any convenience, the PLZT composition of $(Pb_{1-x}, La_x)(Zr_{1-y}, Ti_y)O_3$ is abbreviated as PLZT(x/1 − y/y).

Yoon et al. reported PLZT thin film depositions using a sol–gel method on various single crystal substrates but had no report on EO properties [2]. Nashimoto et al. [3] and Ishii et al. [4] reported EO properties of PLZT thin films. However, their results were not sufficient for fabricating actual integrated EO devices because their linear EO coefficient (Pockels coefficient) was as low as 50 pm/V, which is almost 10% of that of bulk PLZTs (523–612 pm/V) [1]. Haertling also reported a 0.6 μm-thick polycrystalline PLZT(8/65/35) film with a Pockels coefficient of 53 pm/V [5]. In turn, for bulk PLZTs, Oshima and Tsuzuki reported an extremely high Pockels coefficient of 1000 pm/V for PLZT(8/65/35) using a two-step annealing [6]. Thus, achieving higher EO coefficients of PLZT thin films is indispensable and we believe depositing high quality PLZT thin films is the key to obtain higher EO performances.

The other issue for fabricating integrated EO devices is a production cost. Most of recent reports for high quality PLZT deposition are using $SrTiO_3$ (STO) as a substrate [2–4]. However, STO substrates are expensive comparable to substrates that are used in mass-production, e.g. sapphire and silicon. Thus, we adopt sapphire substrates and established the highly (1 0 1)/(0 1 1) oriented PLZT thin films [7].

For high quality oxide depositions, Mizuta et al patented an epitaxial growth of Fe_2O_3 thin films using a methanol pre-treatment of substrates [8]. According to them, the absorbed methanol on substrates might enhance the alignment of precursor molecules and bring the epitaxial growth of oxide films. Based on this idea, we proposed the addition of methanol into the PLZT sol–gel solution as a secondary solvent and achieved epitaxially grown PLZT thin films with a higher EO

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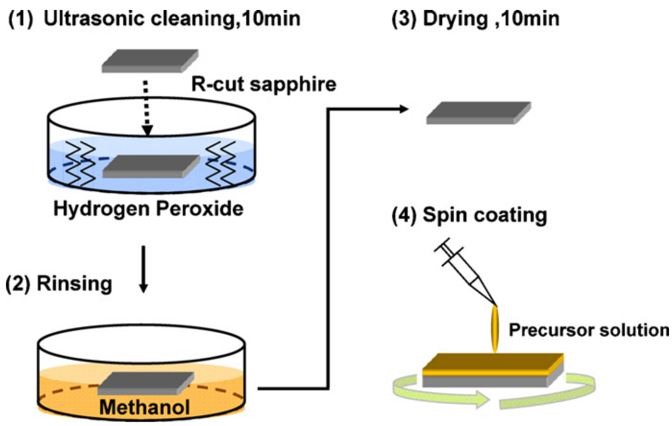

Fig. 1. Schematic process flow of methanol pre-treatment of substrates.

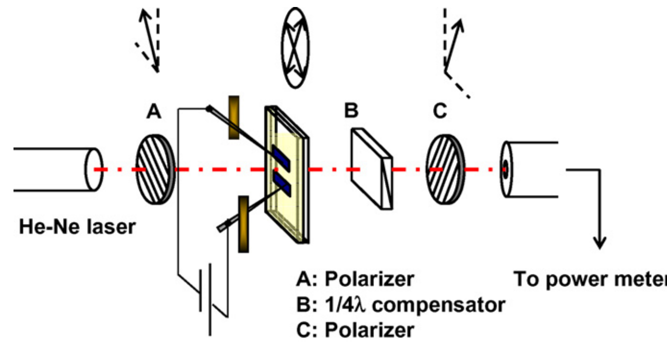

Fig. 2. Schematic configuration of EO measurement system.

property [9]. However, the detailed conditions for the secondary solvent addition and methanol pre-treatment processes were not discussed yet.

In this paper, the effects of solvent addition process other than methanol and the methanol pre-treatment of substrates for high quality PLZT depositions will be described.

2. Experimental procedure

The fabrication procedure of PLZT thin film is a spin-on process using a PLZT mixed sol–gel solution. Detailed fabrication procedure is described elsewhere [7,9]. All of the substrates used in our experiments are r-cut sapphire and cleaned in hydrogen peroxide before deposition. As for the methanol pre-treatment of substrates process, sapphire substrates were rinsed in pure methanol and dried in air (Fig. 1) after the normal substrate cleaning.

The composition of the PLZT precursor (Mitsubishi Materials Co.) was chosen as Pb/La/Zr/Ti = 115/8/65/35 to achieve stoichiometric PLZT(8/65/35) thin films. The precursor concentrations were adjusted as 9 wt.% with *n*-propanol solvent in order to realize high quality depositions [7]. In case of the secondary solvent addition process, a *n*-propanol (90 vol.%)/ secondary solvent (10 vol.%) mixture solution was utilized as a diluting solution instead of using pure *n*-propanol.

Before depositing PLZT films, a $PbTiO_3$ (PT) thin film (about 10 nm thickness) was deposited as a seed layer using sol–gel method in order to provide the nucleation site for perovskite phase [10–13]. The sol–gel solution of PT solution (Mitsubishi Materials Co.) is with 1 wt.% precursor concentration.

After spinning-on PT layer, a PLZT precursor was deposited and dried at 85 °C and decomposed at 350 and 450 °C. This spin-on process was repeated several times until it got 500 nm in thickness. Finally, the deposited PLZT films were sintered at 700 °C for 30 min in air to crystallize.

The crystallographic feature of deposited films was analyzed by X-ray diffraction (XRD) using Cu Kα. EO properties were measured using cross-nicole type measurement configuration (Fig. 2). The platinum (Pt) electrodes with a 300–330 μm gap were deposited on the PLZT thin films for applying the electric fields. Using a He–Ne laser (wavelength: 633 nm), the angle between two polarizers that gave a minimum photo detection with applying various voltages was measured. Based on the measured angle mentioned above, the birefringence, δn, of the PLZT films was calculated. Detailed calculation procedure was in our previous papers [7,9].

3. Results and discussion

Prior to examine the secondary solvent and methanol pre-treatment effects, a seed layer effect on crystallinity of PLZT thin films was measured. The XRD profiles of the PLZT thin films deposited (a) with and (b) without a PT seed layer are shown in Fig. 3. As shown in Fig. 3, the PLZT diffraction of the sample without the seed layer shows lower peak intensity. In turn, the film with the seed layer shows an extremely highly

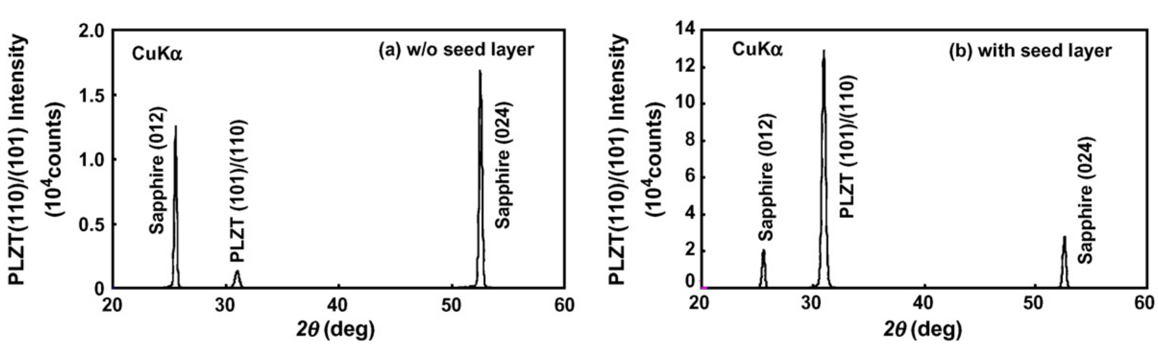

Fig. 3. XRD profiles of the samples derived by with and without seed layers.

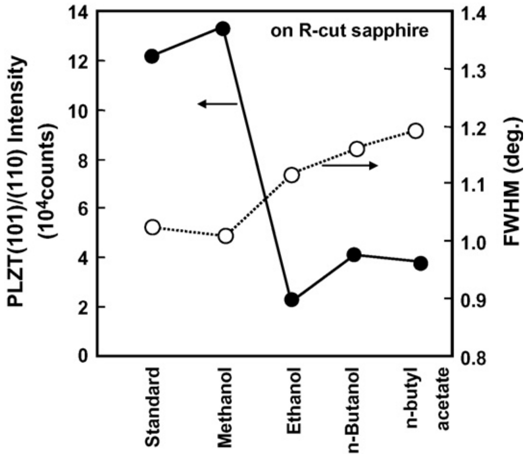

Fig. 4. The variation of the (1 0 1)/(1 1 0) peak intensity and its FWHM value of the samples deposited by various secondary solvent addition processes.

(1 0 1)/(1 0 1) oriented profile with a narrower peak. This result suggests that the seed layer provides the nucleation site and improves crystallinity of the PLZT thin films. Thus, we adopt the PT seed layer in all of our experiments unless it notifies.

Subsequently, the secondary solvent addition effect was investigated for various solvents, such as methanol, ethanol, *n*-butanol, and *n*-butyl acetate. Fig. 4 shows the XRD profiles of the samples derived by the secondary solvent addition processes. The standard process, i.e. no secondary solvents addition, is also described in Fig. 4 as a reference and solid and broken lines are provided for sight.

In Fig. 4, only methanol addition process shows higher peak intensity and narrower FWHM compared to those derived by the standard process. The mechanism with the only methanol addition shows the improvement. It is uncertain if other secondary solvents caused degradation of the film quality, however, it might come from the difference of molecule polarity of the solvents. The secondary solvent addition with higher polarity like methanol might enhance the alignment of sol–gel molecule of PLZT precursors and bring higher crystallinity.

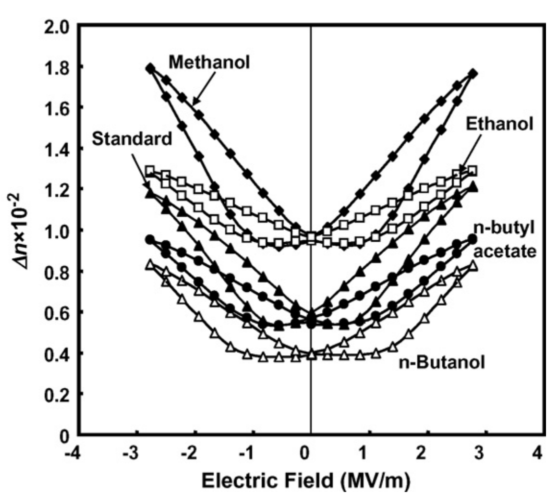

Fig. 5. EO profiles of the samples derived by various secondary solvent addition processes.

Table 1
Summary of Pockels coefficients of the films derived by secondary solvent added processes

	Pockels coefficient (pm/V)	
	Forward side	Backward side
Standard	495	268
Methanol	717	406
Ethanol	257	162
n-Butanol	387	237
n-Butyl acetate	305	191

The variations of birefringence, δn, according to applied electric fields for the samples derived by various secondary solvent are shown in Fig. 5. Their Pockels coefficient is also summarized in Table 1. Based on these results, only methanol addition improves Pockels coefficients. This may come from the difference of the film crystallinity of PLZT thin films. As a consequence, we confirm that the only methanol addition is effective to improve PLZT film crystallinity and the EO property.

Finally, the effects of the methanol pre-treatment of substrate on crystallinity and EO property were examined. Fig. 6 shows reciprocal space mappings for the samples derived by standard, methanol added, and methanol pre-treated processes. The XRD patterns of these samples are extremely highly (1 0 1)/(1 1 0) oriented, however, the reciprocal space mapping reveals that the samples derived by methanol added and methanol pre-treated processes are epitaxially grown, though the sample derived by the standard process is polycrystalline. This implies that both of the methanol added and the methanol pre-treated processes are quite effective to achieve epitaxially grown PLZT thin films. The Pockels coefficients of these samples are summarized in Table 2. All of the Pockels coefficient in forward side is as high as that of bulk PLZTs [1,7], however, methanol added and methanol pre-treated processes bring higher Pockels coefficients compared to that of the standard process. Especially, the sample derived by methanol added process shows a high Pockels coefficient of 717 pm/V for forward side, which is higher than those of conventional bulk PLZTs [1]. These results suggest the methanol addition and pre-treatment of substrate are quite effective for improving film crystallinity and EO property.

Table 2
Summary of Pockels coefficients of the films derived by methanol treatment processes

	Pockels coefficient (pm/V)	
	Forward side	Backward side
Standard	495	268
Methanol added	717	406
Methanol pre-treated	532	362

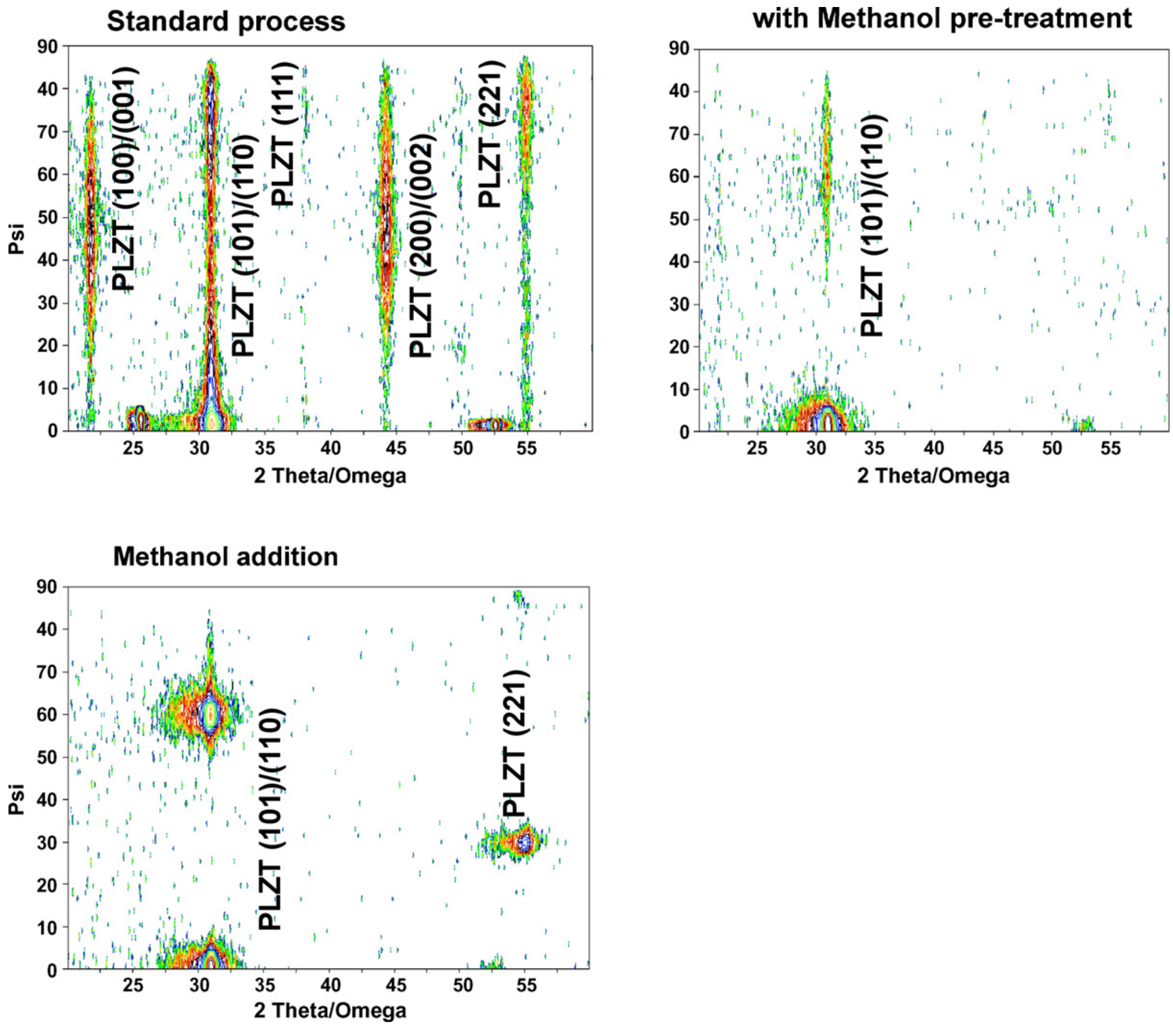

Fig. 6. Reciprocal mappings of the samples deposited by standard, methanol pre-treated, and methanol added processes.

4. Conclusions

In this paper, we described various deposition processes to improve PLZT film qualities. First of all, the role of the PT seed layer was demonstrated and it is confirmed that the PT seed layer is indispensable for highly oriented PLZT depositions. Second, secondary solvent addition process was discussed and it is found that only methanol addition improves the film crystallinity and the EO property. Finally, the effect of methanol pre-treatment of substrates on film characteristics was also mentioned.

Through these optimizations, epitaxially grown PLZT thin films on r-cut sapphire was obtained and high Pockels coefficient comparable to those of bulk PLZTs was achieved. It is believed that these PLZT thin films are applicable for integrated EO devices and open the door for the future data communication systems.

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