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Effect of Seeding Layers on Preparation of PLZT Thin Films by Sol-Gel Method

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$(Pb_xLa_{1-x})(Zr_yTi_{1-y})O_3$ (PLZT) thin films with electrooptic effect are promising for the optical applications such as display or light shutter However, it is difficult to use inexpensive and transparent glass substrates because the conventional process for preparation of PLZT requires temperatures above 600°C. In order to deposit a perovskite PLZT thin films at low processing temperatures through alkoxide route, we have offered several seeding processes which reduce the activation energy for crystallization. In this study, we optimized the stacking structure of multi-layered PLZT for obtaining single phase perovskite at lower temperatures. As a result, ferroelectric PLZT thin films with different compositions were successfully prepared at a temperature as low as 500°C.

Key words : PLZT, PLT, Perovskite, Ferroelectricity, Seeding layer

I. Introduction

PLZT is a transparent ceramic which was developed by Heartling in 1971.[1] PLZT is one of the most promising material for optical devices such as light shutter and display because it exhibits both Kerr and Pockels effects. To apply PLZT for the optical devices, a single phase perovskite PLZT is required. If the PLZT thin films are prepared by wet chemical processing, they crystallized into perovskite phase via pyrochlore. However, the pyrochlore phase does not exhibit the desired optical effects.[2] Therefore, single phase perovskite structure is required for PLZT films.

Commercial PLZT has been prepared by hot-pressing at above 600°C, resulting in high cost.[3] For thin film processing, sputtering[4] and sol-gel method have been studied. Lee *et al.* reported[5,6] low temperature processing of PLZT thin films by sol-gel method. However, the optimum composition for the electrooptic effect was not obvious. In addition, high-temperature annealing above 600°C was required to obtain single phase perovskite for the Zr rich composition.

This paper focuses on the low-temperature processing of PLZT thin films with different compositions which shows the electrooptic effect by the seeding process. If a low-temperature process is established, various substrates with low melting temperatures can be used, leading to the wide or new applications. To demonstrate this, commercial soda-lime glass with transparent indium tin oxide (ITO) electrode was used as a substrate. Compositions of PLZT studied were in the range from Ti rich to Zr rich compositions (20<Zr<65, 35<Ti<80), which were expected to show the electrooptic effect.

Many parameters such as the substrate, temperature, annealing and the atmosphere affect the crystallization behaviour of PLZT thin films. Among them, seeding process is one of the most effective method to lower the crystallization temperature.[7,8] Therefore, we used seeding layer to introduce the nucleation sites, which lowered the activation energy for the crystallization. We offered two types of seeding processes for the PLZT thin films.

II. Experimental Procedure

Fig. 1 indicates the preparation method of PLZT and $Pb_xLa_{1-x}TiO_3$ (PLT) precursor solutions. Lead acetate, lanthanum acetate, zirconium i-propoxide and titanium i-propoxide were used as raw materials. In this study, the compositions for PLZT and PLT precursors are described as (100-100x/100y/100-100y) and (100-100x/100)), respectively. For PLZT precursor, (10/65/35), (15/53/47), (20/20/80), and PLT precursor, (10/100), (15/100), (20/100) were prepared. The solvent was 2-methoxyethanol and the concentration of cation was 0.6M. Soda lime glass of 1.1 mm thickness with dip-coated sol-gel derived SiO_2 for passivation layer was used as a substrate. Then, ITO (215 nm) was coated on the substrate to give sheet resistance in the range 9.0~9.5Ω/□ (ITO/Glass). In some experiments, PLZT thin film was deposited on Si wafer to investigate the effect of different substrates on the crystallization behaviour.

Dip-coating method was used for the film deposition,

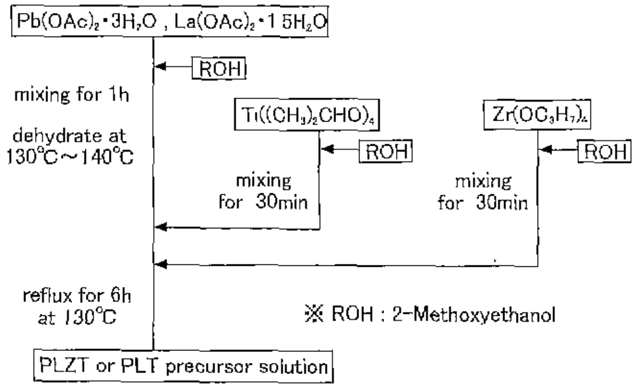

Fig. 1. Flow diagram for the synthesis of PLZT or PLT precursor solution.

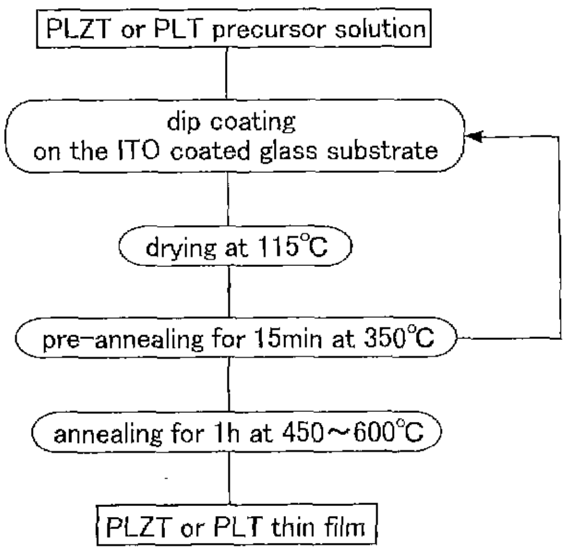

Fig. 2. Flow diagram for the preparation of PLZT or PLT thin film.

with the withdrawal speed of 0.1 mm/min. Film thickness was estimated from Scanning Electron Microscope (SEM) images of the cross sections. Estimated thickness for one coating was about 50 nm. The as-deposit film was pre-annealed at 350°C for 15 min followed by the annealing at 450, 500 or 600°C for 1 hour (Fig. 2).

In this study, two different types of seeding methods were used. One was a single seeding process and the other was a multi- seeding process,[7-9] where the seeding layers of PLT and PLZT layers were deposited alternately. The cross sections of the stacked structure are illustrated in Fig. 3.

The crystalline phases developed during annealing were identified by X-ray diffraction (XRD; Rigaku RINT 2000).The transmittances of the samples were measured by UV-Visible Spectroscopy (Shimazu UV-3520). The ferroelectric properties of some samples were measured by RT-6000S (Radiant Technology Inc.) using gold upper electrode.

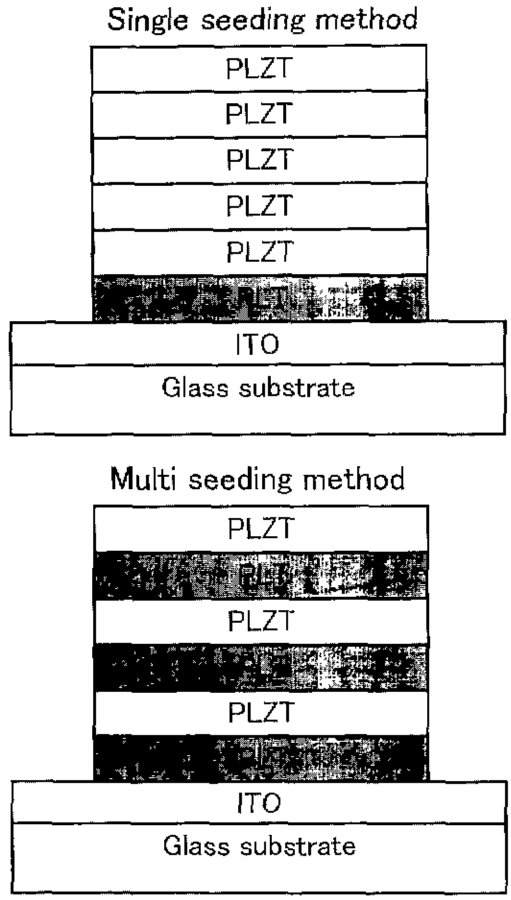

Fig. 3. Illustration of stacking structure for single-seeding or multi-seeding process.

III. Results and Discussion

1. Crystallization behaviour of precursor

The crystallization behaviour of PLZT and PLT precursors on ITO/Glass were investigated and shown in Fig. 4 and 5. As shown in Fig. 4, only the ITO peaks were observed up to 500°C. A single phase perovskite thin film was deposited for the (20/20/80) composition at 600°C. However, for the (15/53/47) composition, a mixture of perovskite and pyrochlore was identified, and only the pyrochlore phase was observed for the Zr rich (10/65/35) composition at 600°C. These results indicate that perovskite phase in the PLZT precursor film tends to crystallize at lower temperature with increasing Ti concentration. This tendency has been confirmed by the other studies.[5] Although the single phase perovskite was obtained at 600°C for Ti rich (20/20/80) films, this temperature was still high when the ITO/Glass was used as a substrate. The degradation of substrate at this temperature leads to the reduced electrical properties of the resultant films. Fig. 5 shows the crystallization behaviour for PLT precursor.

For the PLT thin films, perovskite phase was identified at above 500°C. However, sol-gel derived $PbTiO_3$ film crys-

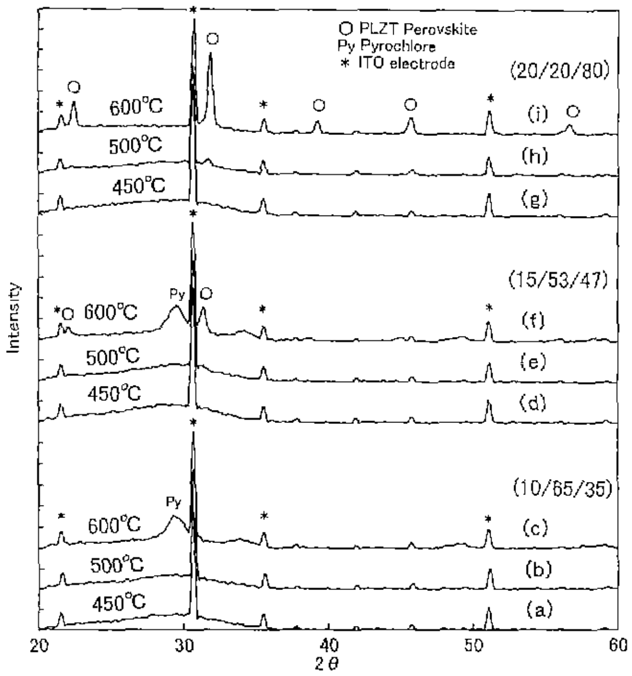

Fig. 4. XRD patterns of PLZT thin films on ITO/Glass without seeding (a), (b) and (c) are the XRD patterns of the composition (10/65/35), annealed at 450, 500 and 600°C respectively, (d), (e) and (f) are the XRD patterns of the composition (15/53/47), annealed at 450, 500 and 600°C respectively (g), (h) and (i) are the XRD patterns of the composition (20/20/80), annealed at 450, 500 and 600°C respectively.

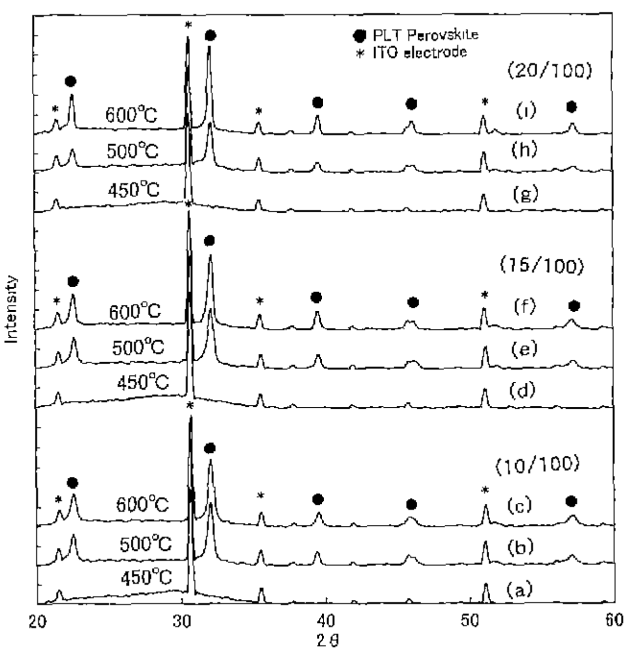

Fig. 5. XRD patterns of PLT thin films on ITO/Glass without seeding (a), (b) and (c) are the XRD patterns of the composition (10/100), annealed at 450, 500 and 600°C respectively (d),(e) and (f) are the XRD patterns of the composition (15/100), annealed at 450, 500 and 600°C respectively (g), (h) and (i) are the XRD patterns of the composition (20/100), annealed at 450, 500 and 600°C respectively.

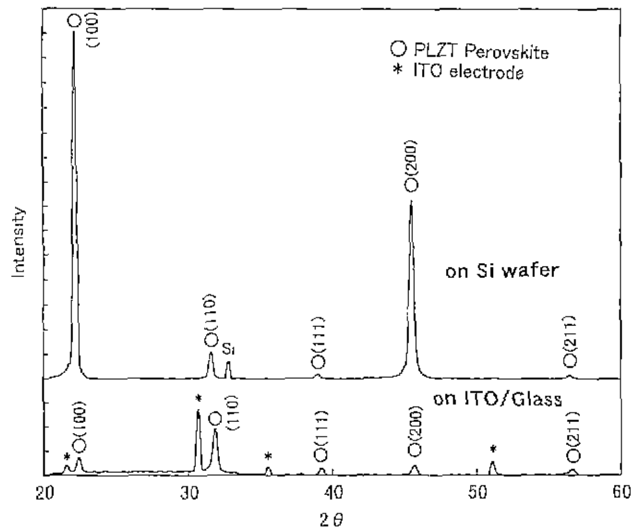

Fig. 6. XRD patterns of PLZT(20/20/80) thin films annealed at 600°C on different substrates of Si wafer or ITO/Glass without seeding.

tallized into perovskite phase at 450°C.[8] Therefore, it can be concluded that addition of La increases the crystallization temperature of perovskite phase for $PbTiO_3$ film.

2. *Effect of substrate*

One of the parameters affecting the crystallization behaviour of PLZT thin film is the substrate. The crystallization behaviour of PLZT thin films on ITO/Glass and Si wafer investigated at 600°C (Fig. 6). As shown in Fig. 6, PLZT thin film on Si wafer exhibited the orientation to (100) direction, whereas PLZT thin film on ITO/Glass exhibited perovskite phase with random orientation. The random orientation of the PLZT films on ITO/Glass is ascribed to the lattice mismatch between ITO and PLZT. On the other hand, the reason for (100) orientation of the PLZT thin film on Si wafer is not clear. However, this seems to be related to the (100) orientation of Si wafer.

It is considered that c-axis orientated PLZT thin film with perovskite type structure exhibit the excellent electrical properties. Crystallization behaviour of PLZT precursor in this study was strongly affected by the type of the substrate.

3. *Effect of seeding layer*

From the results in section (1), PLT seems to be an excellent candidate as a seeding layer because a single phase perovskite films were deposited at 500°C. Therefore, PLT precursor with same Zr/Ti ratio as PLZT which suppresses the composition change of the resultant films after annealing was selected as seeding layer. The crystallinity of the seeding layer also has large effect on the crystallization of PLZT films. Fig. 7 shows the XRD patterns for (10/65/35) PLZT thin films with seeding layers of different thickness and crystallinity. In this figure, a seeding layer was pre-annealed at 350°C (in situ seeding)

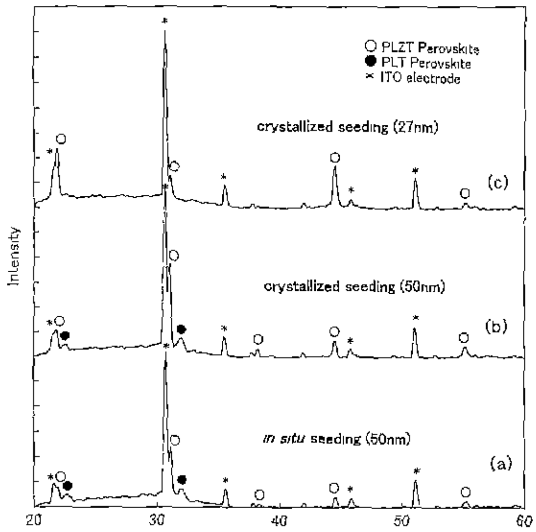

Fig. 7. XRD patterns of PLZT(10/65/35) thin films on ITO/Glass annealed at 500°C by single seeding process. PLT seeding layer pre-annealed at 350°C (a) or 500°C, (b) with 50 nm thick and pre-annealed at 500°C with 27nm thick (c).

and other seeding layers were pre-annealed at 500°C to obtain the well-crystallized seeding layers (crystallized seeding). All PLZT films with seeding layer had perovskite structure at 500°C, even for the Zr rich composition (Fig. 7).

This suggests that seeding layer lowers the activation energy for crystallization of perovskite phase. In addition, PLZT film with 500°C annealed seeding layer showed higher crystallinity (Fig. 7(b)), leading to superior electrical properties (Fig. 9). In this case, different peaks corresponding to the PLT seeding layer were identified. Therefore, we prepared PLZT film with thin seeding layer (Fig. 7(c)). As a result, diffraction peak of PLT was not identified and the resulting PLZT film oriented to (100) direction. This result is consistent to that of Lee *et al.*[5] Insertion of well-crystallized thin seeding layer preannealed at 500°C between PLZT film and substrate resulted in the low-temperature deposition of c-axis oriented PLZT film. On the other hand in multi-seeding process, both PLT and PLZT perovskite were identified at 500°C (Fig. 8). This suggests that the resultant films were consisted of alternative stacking of PLT and PLZT perovskite layers. PLT layers did not dissolve into PLZT layers to form solid solutions at this temperature. Molecular

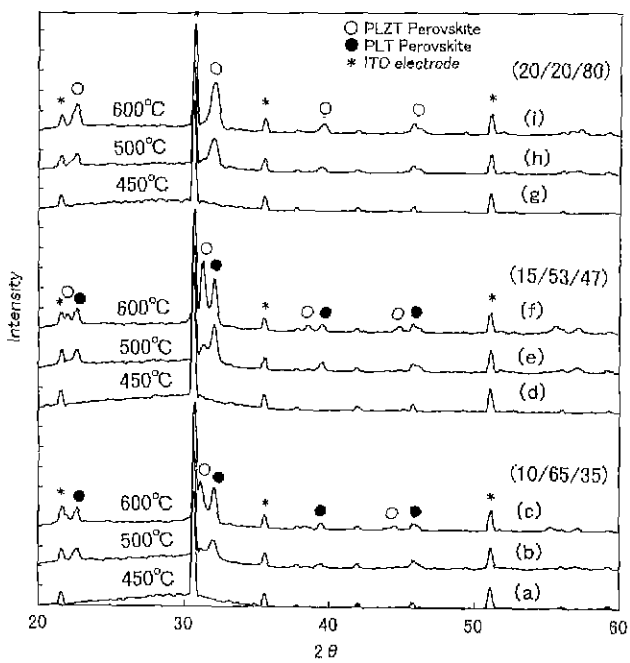

Fig. 8. XRD patterns of PLZT thin films on ITO/Glass by multi seeding process (a), (b) and (c) are the XRD patterns of the composition (10/65/35), annealed at 450,500 and 600°C respectively (d), (e) and (f) are the XRD patterns of the composition (15/53/47), annealed at 450, 500 and 600°C respectively (g), (h) and (i) are the XRD patterns of the composition (20/20/80), annealed at 450, 500 and 600°C respectively.

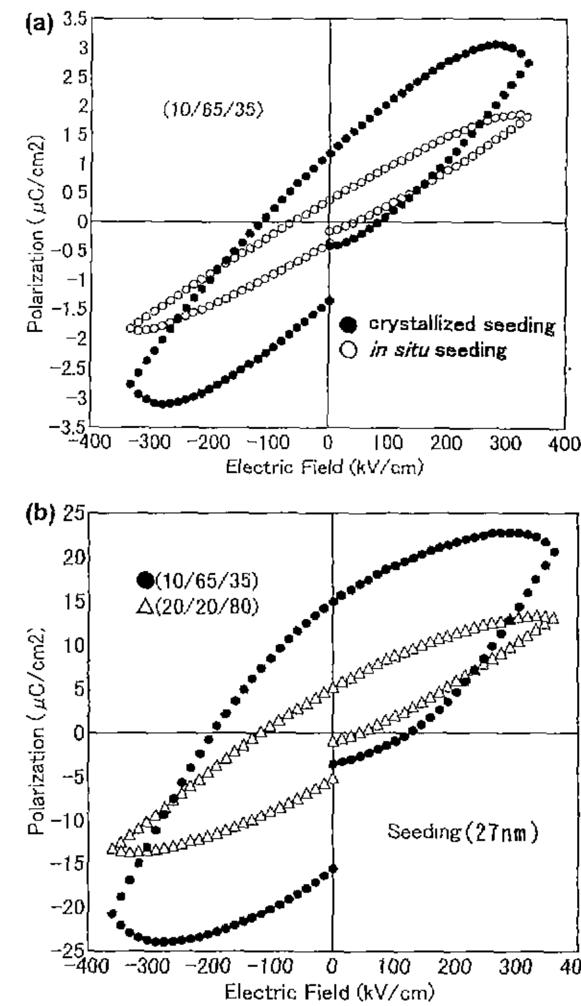

Fig. 9. P-E hysteresis loops for PLZT thin films annealed at 500°C on ITO/Glass by single seeding process (a) P-E hysteresis loops for PLZT thin films for the composition (10/65/35) with seeding layer thickness of 50 nm (b) P-E hysteresis loops for PLZT thin films for the different compositions and seeding layer thickness of 27 nm.

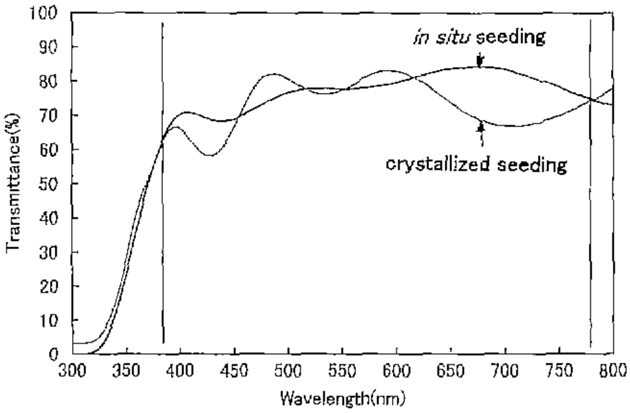

Fig. 10. The transmittance spectra of PLZT films with (20/20/80) composition annealed at 500°C.

design of precursor solutions for PLT and PLZT is essential to prepare single phase PLZT by multi-seeding process.

4. Electrical and optical properties of thin film

As already described above, single phase perovskite type PLZT thin films were succesfully deposited onto ITO/Glass at low temperature of 500°C in the wide range compositions. In this section, ferroelectricity and transmittance of the resultant films were measured. Fig. 9 shows the P-E hysteresis loops for low-temperature processed PLZT thin films. As a result, PLZT films with well-crystallized seeding layer exhibited higher remanent polarization (Fig. 9(a)). However, hysteresis loops did not show enough saturation. Higher applied field is essential to obtain the good hysteresis loops for the PLZT thin films, showing the relatively large leakage current of the resultant films. This also may be ascribed to the crystallinity of the resultant films. Further investigation is indispensable to improve the film quality. In addition, PLZT film with thin seeding layer exhibited superior ferroelectricity compared to the PLZT film with thick seeding layer (Fig. 9(a) and (b)). This result confirmed the crystallization behaviour (Fig. 7) Increased remanent polarization for the PLZT film with thin seeding layer is ascribed both to the orientation and crystallinity of the resultant films. On the other hand, remanent polarization decreased with increasing Ti content (Fig. 9(b)). However, low coercive field was obtained in the case of PLZT film with Ti rich composition of (20/20/80). Therefore, we have to change the compositions depending upon the objectives.

Figure 10 shows the transmittance of the resultant PLZT films. As shown in the figure, more than 60% of transmittance was attained in the visible region for all films. This indicates the possibility for applying the low-temperature processed PLZT films in optical devices.

IV. Conclusions

This paper focused on the preparation of PLZT thin films at low temperatures by using seeding process. From the comparison of different seeding processes, followings are concluded;

(1) Perovskite formation temperature for PLZT thin films decreased with increasing Ti content.

(2) Perovskite formation temperature for PLT thin films were higher than PT thin film and lower than PLZT thin films. Increased amount of La addition resulted in the higher perovskite formation temperature.

(3) Single-seeding process is effective for low-temperature processing of PLZT thin films.

(4) Insertion of well-crystallized thin seeding layer between PLZT precursor film and substrate resulted in the (100) oriented perovskite PLZT thin films at low temperature of 500°C.

(5) Low-temperature processed PLZT thin films showed relatively good ferroelectricity and transparency more than 60% transmittance in the visible region.

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