Influences of Seeding Layer on Physical Properties of PLZT Thin Film Grown by Sol-gel Method

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Abstract

Sol-gel-processed PLZT thin films were prepared on indium tin oxide-coated glass substrate. The composition in this study was $Pb_{0.92}La_{0.08}Zr_{0.65}Ti_{0.35}O_3$. *PLT films used as seeding layers offered nucleation sites to reduce the activation energy for the crystallization. The films were fabricated by dip coating and heat-treated at different temperatures from 600°C to 700°C. The phase and microstructure of PLZT thin films were characterized by X-ray Diffraction (XRD) and Scanning Electron Microscopy technique (SEM). The PLZT thin film with PLT seeding layer improved perovskite phase content and enhanced perovskite transformation kinetics. PLZT films with dense and homogeneous microstructure were obtained. The grain sizes of the PLZT thin film with PLT seeding layer were reduced from 5 μm to 0.1 μm. The PLZT thin films with seeding layers showed good ferroelectric properties such as large remanent polarization and high dielectric constant.*

Keywords: PLZT, Thin films, Sol-gel, seeding layers

Introduction

Lead oxide based ferroelectric films have been investigated for a variety of device applications including electro-optic devices and non-volatile Random Access Memories (RAMs) [1, 2]. Lanthanum doped lead zirconate titanate (PLZT) is a candidate material for these applications because it exhibits slim hysteresis loop as compared to unmodified lead zirconate titanate (PZT) [3].

Sol-gel processing offers several potential advantages for forming thin films such as high purity, chemical homogeneity, low crystallization temperature, inexpensive equipment, and its ease of fabrication. However, previous works demonstrated that it has been difficult to prepare phase-pure perovskite PLZT thin films. Sol-gel derived PLZT first crystallized upon heating to an intermediate phase at low temperature before transforming to the perovskite structure. Since the crystal structure of pyrochlore is a Pb-deficient structure, small volume percentages of residual intermediate phase or pyrochlore phase can be detrimental for the film quality.

The processing techniques proposed to reduce the pyrochlore problem are an addition of excess Pb in precursor solution [4] and seeding layers for perovskite crystallization [5, 6]. The excess Pb was added to compensate for lead-loss on heat treatment. The use of seeding layers which have a lower crystallization temperature, such as $PbTiO_3$, $PbLaTiO_3$ can lead to crystallization of PLZT films at reduced temperature.

In this work, Sol-gel derived PLZT films were prepared on indium tin oxide (ITO)–coated glass substrates. PLT thin films were used as the seeding layer. Excess Pb (10% mole) was added to PLZT solution. Compared with PLZT thin films with and without seeding layer, the effects of seeding layers on phase transformation, microstructure, and electrical properties were investigated.

Experimental details

The preparation of stock solutions was carried out by sol-gel technique [2]. Fig. 1 shows the flow chart for complete PLZT film preparation including the sol-gel process. Lead acetate trihydrate ($Pb(CH_3COO)_23H_2O$; 99% Aldrich), lanthanum acetate hexahydrate ($La(CH_3COO)_36H_2O$; 99% Aldrich), zirconium n-propoxide ($Zr(OCH(CH_3)2)4$; 97% Fluka) and titanium isopropoxide ($Ti(OCH(CH_3)_2)_4$; 97% Fluka) were used as starting precursors, with 2-methoxyethanol ($CH_3OCH_2CH_2OH$; 99% Aldrich) as a solvent. Lead acetate trihydrate and lanthanum acetate hexahydrate were separately dissolved and distilled in 2-methoxyethanol at 125°C for water elimination. In order to compensate for Pb loss on heat treatment, an addition 10% Pb excess in solution was used. The dehydrated solution was mixed with 0.65 mol of zirconium n-isopropoxide and 0.35 mol of titanium isopropoxide in a glove box. The mixture was then refluxed at 90°C for 4-5 hours under flowing argon gas in order to promote dissolution. Water was added for hydrolysis reaction, followed by formamide to prevent cleavage of the films. A 0.4 M stock solution was finally obtained.

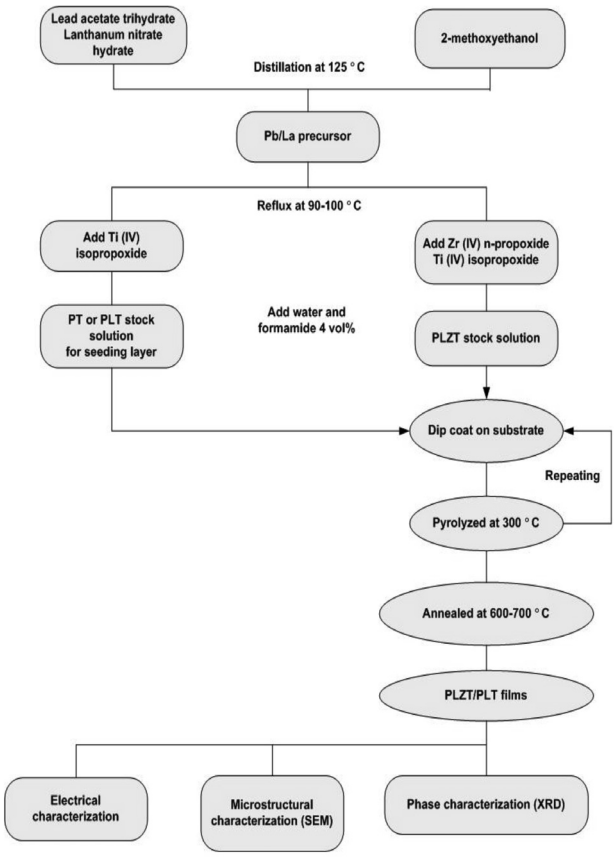

Fig. 1. Flow chart for PLZT film preparation.

To prepare the PLT solution as a seeding layer, lead acetate trihydrate, lanthanum acetate hexahydrate, and titanium isopropoxide were used as starting precursors, with 2-methoxyethanol as a solvent. The procedure of the solution preparation was similar to that of PLZT solution. The PLT solution with 0.15 M was coated once before PLZT coating. ITO-coated polished Corning glass (Delta Technologies company) was used as substrate. The substrate was cleaned by immersion in isopropanol. The 0.5 μm syringe filter was used to avoid a particulate contamination. The deposition of the films was performed by dip coating. The film was pyrolyzed on a hot plate for 2 minutes in air at 200°C. The sequence dip coating-pyrolysis was repeated until the required film of 0.5 μm thickness was obtained. The films were annealed in a box furnace at various temperatures with a heating rate of 20 °C/min.

The microstructural developments were investigated by scanning electron microscope (SEM; JEOL JSM-5410). Phase identification of the annealed films was performed using X-ray diffractometer (Rigaku DMAX) at a glancing angle of 5°C. The ferroelectric properties were measured by using an RT66A ferroelectric tester (Radiant technologies).

Results and discussion

Morphological features of sol-gel-derived PLZT (8/65/35) films without and with seeding layers inserted between the films and ITO coated glass substrates are shown in Fig. 2. Microstructural changes were observed for the films annealed between 600°C and 700°C.

Fig. 2 (a)-(c) shows SEM micrographs of the films without a seeding layer annealed at 600°C, 650°C, and 700°C. The film annealed at 600 °C appeared diphasic.

The phase of bright contrast had the spherical feature (~5μm diameter). This feature, known as the rosette structure, in the film without a seeding layer (Fig. 2(a)), is perovskite phase. The remaining phase surrounding the rosette structure is metastable pyrochlore phase. The films annealed at 650°C and 700°C also appeared diphasic (Fig. 2(b)-(c)). They contained a larger volume fraction of rosette phase. The average rosette diameter of the films was smaller than that for the 600°C film.

Fig. 2 (d)-(f) shows SEM micrographs of the films with a seeding layer annealed at 600°C, 650°C, and 700°C. Insertion of PLT layer between the films and the substrate brought about significant morphological changes. The film annealed at 600°C appeared featureless. After heat treatment at 650°C, the films shows that formation of PLT interlayer resulted in reduction of the grain size and the rosette structure disappeared. The film annealed at 700°C shows dense and homogeneous microstructure with reduced grain size of 0.1 μm.

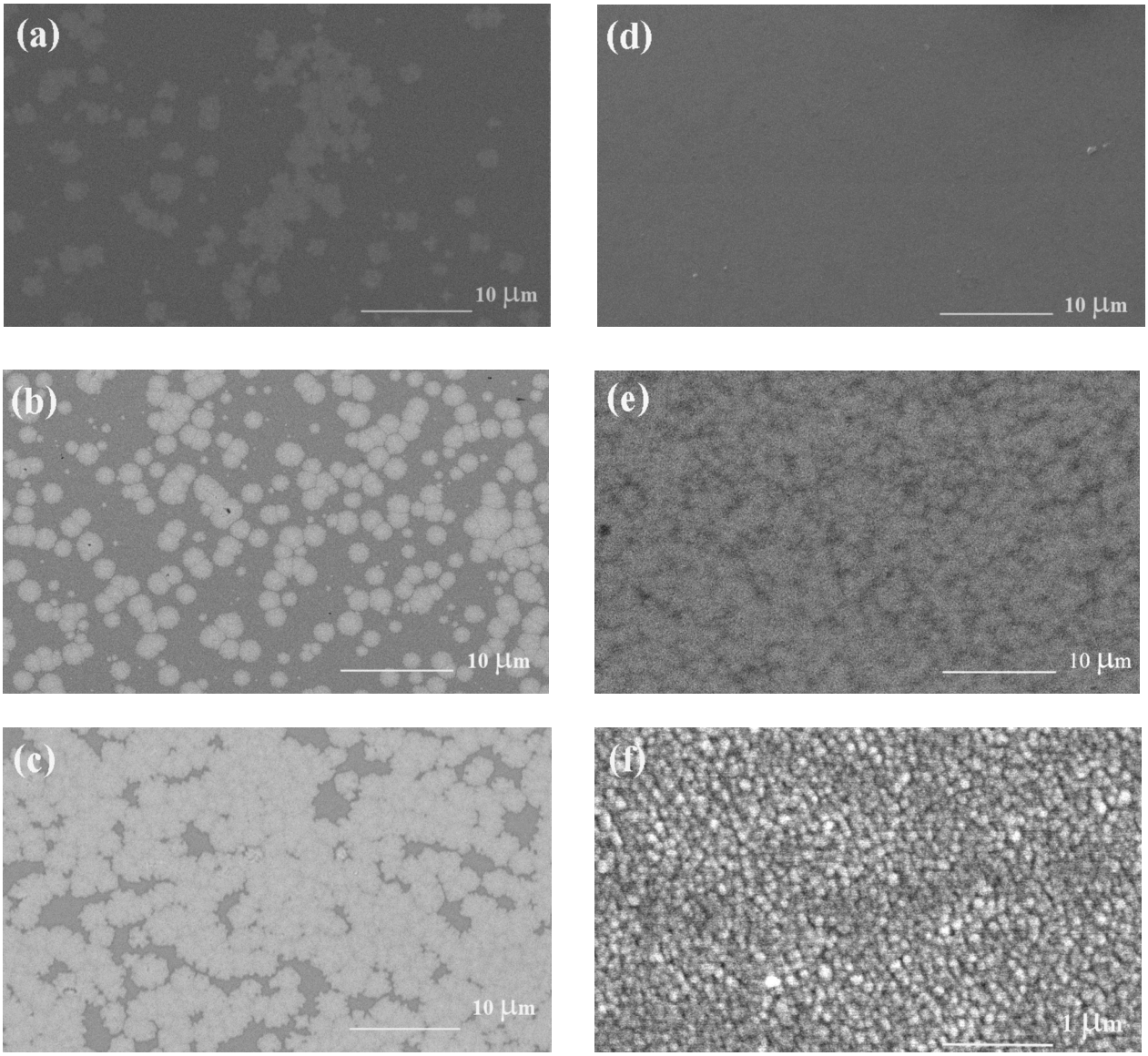

Fig. 2. SEM photographs of the PLZT films (a-c) without and (d-f) with the PLT seeding layer annealed at (a,d) 600°C, (b,e) 650°C and (c,f) 700°C, 30 min.

X-ray diffraction studies were performed on PLZT films deposited on ITO coated glass substrates. Fig. 3 shows XRD patterns of the PLZT (08/65/35) films without and with a PLT seeding layer (SL) prepared at annealing time 30 min. In the case of films without seeding layers, perovskite, pyrochlore and ITO peaks used as a substrate were observed at 650°C. Perovskite phase could not be obtained as a single phase by heat treatment at 700°C. The films still retained the pyrochlore phase at higher annealing temperature (700°C). In the case of films with PLT a seeding layer annealed at 650°C, perovskite phase became predominant. Further increase of annealing temperature to 700°C resulted in the disappearance of pyrochlore phase. The ratio of perovskite to pyrochlore contents of the films increased by applying a seeding layer between the films and substrate.

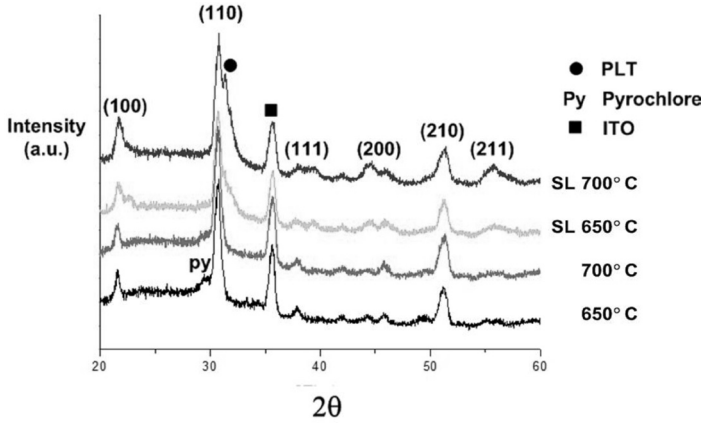

Fig. 3. XRD patterns of the PLZT (08/65/35) films without and with PLT seeding layer prepared with annealing time of 30 min.

During the annealing process, the amorphous films were first transformed into pyrochlore at a temperature range of 400-500°C, and then transformed into perovskite at above 500°C. As the annealing temperature above 650°C, Pb started to evaporate and then the composition of films changed by Pb loss. This resulted in the formation of pyrochlore phase or Pb-deficient phase [7]. In the case of direct growth of the PLZT films upon the substrate, the films showed a microstructure characterized by a rosette (perovskite) structure surrounded by a fine-grain (pyrochlore) matrix [8]. The surface morphology of the films without the seeding layer may be influenced by the reduction of perovskite content.

In contrast, PLT seeding layer has an impact on the crystallization and microstructure. PLT, Ti-rich phase, can directly transform into stable perovskite phase at low temperature (about 500°C), whereas Zr-rich materials, PLZT, transform into pyrochlore phase and then transform to perovskite phase at higher temperature (above 600°C) [9]. Thus, a PLT layer may promote higher perovskite content by increasing the number of active sites for PLZT nucleation, and then allow crystallization of perovskite phase in PLZT films. Films with dense and uniformly small grain size can be obtained. A smaller number of perovskite nuclei may form in a film without the seeding layers.

The P-E hysteresis loop measurements are illustrated in Fig. 4 It can be seen that the film with higher annealing temperature exhibited higher remnant polarization. With a heat treatment at 700°C, the average values for films without a seeding layer were $P_r \sim 11$ μC/cm^2 and $E_c \sim 75$ kV/cm. The average values for the films with a seeding layer were $P_r \sim 28$ μC/cm^2 and $E_c \sim 65$ kV/cm.

A considerable increase in remanent polarization through insertion of PLT layer of PLZT films to reflects an influence of the seeding layers upon microstructural improvement of these films, such as the disappearance of rosette structure and dense, uniform peroskite structure as shown in Fig. 2. A decrease of the coercive of PLZT films due to seeding layer insertion indicated that the resulting films had good crystallinity of perovskite phase, as seen in Fig. 4, and no longer remain a second phase as barriers against domain boundary movement.

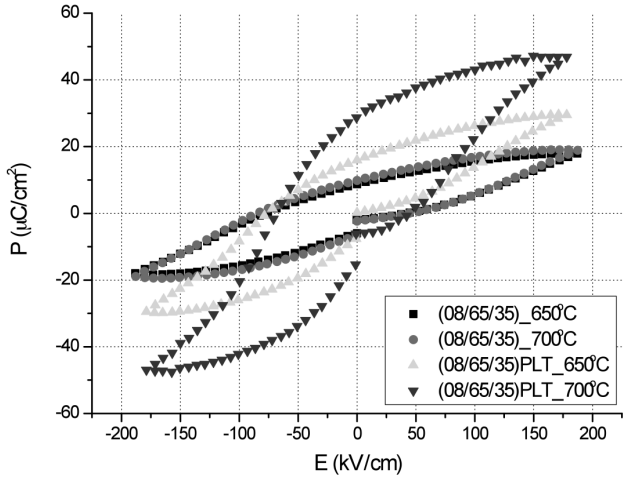

Fig. 4. Ferroelectric hysteresis for the PLZT films without and a with seeding layer annealed at 650-700°C.

Conclusion

$Pb_{0.92}La_{0.08}Zr_{0.65}Ti_{0.35}O_3$ thin films were successfully deposited on ITO coated on Corning glass by a sol-gel process. This study has shown that high quality, single phase perovskite thin films can be prepared by the use of seeding layers, 10%Pb excess in precursor solution, and annealing at 700°C. The experimental results revealed that the insertion of PLT seeding layers led to better ferroelectric properties of the PLZT films by enhancing the perovskite content and uniform microstructure.

Acknowledgements

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