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Fabrication and properties of perovskite $Pb(Yb,Nb)O_3$–$PbTiO_3$ thin films through a sol–gel process

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Abstract

Crack-free $Pb(Yb_{1/2}Nb_{1/2})O_3$–$PbTiO_3$ (PYN–PT) thin films have been fabricated by the chemical solution deposition. Homogeneous and stable PYN–PT precursor solutions were prepared by selecting appropriate starting metal-organic compounds and 2-methoxyethanol as a solvent. The optimization of several processing conditions, such as precise control of composition, heating process and $PbTiO_3$ seed layer, was found to be a key for the crystallization of perovskite PYN–PT films on $Pt/TiO_x/SiO_2/Si$ substrates with good surface morphologies. Synthesized PYN–PT thin films exhibited a ferroelectric *P–E* hystresis loop and the frequency dependence of dielectric constant.

Keywords: PYN–PT; Thin film; Chemical solution deposition; Seed layer; Electrical properties

1. Introduction

Ferroelectric thin films such as $PbZr_{1-x}Ti_xO_3$ (PZT) are highly attractive for several thin film device applications and there has been a growing interest in the development of new materials with better electrical properties. Since single-crystal relaxor ferroelectric-$PbTiO_3$ solid solutions such as $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PMN–PT) and $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ are reported to exhibit excellent properties [1,2], thin film processing also has been studied [3,4]. Furthermore, rare-earth contained relaxor ferroelectric ($Pb(R_{1/2}Nb_{1/2})O_3$ [R: Ho, Yb, Lu])–$PbTiO_3$ solid solutions with a morphotropic phase boundary (MPB) have been receiving great attention. Among them, $(1-x)Pb(Yb,Nb)O_3$–$xPbTiO_3$ (PYN–PT) system is known to have a morphotropic phase boundary (MPB: $x = 0.5$) and the highest Curie temperature (>360 °C), and to show excellent ferroelectric and piezoelectric properties [5,6]. The high Curie temperature should improves the temperature stability of ferroelectric thin film devices fabricated with relaxor-PT solid solutions.

The investigations of the PYN–PT system have been concentrated to the MPB compositions up to now [7–10], because several properties exhibit the maximum at the MPB. However, Foster et al. and Oikawa et al. reported on the ferroelectricity of the MOCVD-derived PZT films with different Zr:Ti ratios [11,12]. They mentioned the P_s and P_r value showed the minimum value near the MPB, whereas the dielectric constant exhibited the maximum at the MPB. In these reports, large P_r values were observed in the tetragonal symmetry region. This tendency is quite different from those of the bulk [5]. Therefore, in this study, PYN–PT thin film with a composition in the tetragonal region was examined.

In general, lead-based relaxor ferroelectric materials are known to be difficult to crystallize in the perovskite phase. The crystallization of PYN–PT phase on substrates results in the formation of low temperature phase of pyrochlore, which exhibits poor electrical properties. However, the crystallization of perovskite PYN–PT at lower temperatures is indispensable in order to fabricate thin films with high quality.

In this paper, ferroelectric $0.3Pb(Yb_{1/2}Nb_{1/2})O_3$–$0.7PbTiO_3$ (PYN–70PT) thin films are synthesized by the chemical solution deposition (CSD), because the CSD process using metal-organic compounds is useful for the

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low-temperature fabrication and the precise control of the chemical composition. The crystallization of perovskite PYN–PT films on Pt/TiO_x/SiO_2/Si substrates is investigated for several processing conditions, including heating process and $PbTiO_3$ seed layer. Ferroelectric and dielectric properties of the synthesized PYN–PT films are also evaluated.

2. Experimental procedure

$Pb(CH_3COO)_2$ and $Ti(O^iPr)_4$ and $Yb(CH_3COO)_3$ and $Nb(OEt)_5$ were selected as starting materials for preparing a PYN–PT precursor solution. $Yb(CH_3COO)_3{\cdot}4H_2O$ was dehydrated at 110 °C for 4 h under vacuum yielding anhydrous $Yb(CH_3COO)_3$. 2-Methoxyethanol was dried over molecular sieve and distilled prior to use. The desired amounts of starting materials with 5 mol% excess Pb were dissolved in absolute 2-methoxymethanol. Acetylacetone was added to the solution as a stabilizing agent. Then, the mixed solution was refluxed for 20 h yielding a 0.1 M homogeneous precursor solution. The entire procedure was conducted in a dry N_2 atmosphere.

Films were fabricated using the precursor solution by spin-coating on Pt/TiO_x/SiO_2/Si substrates. In order to prepare crystalline PYN–PT of perovskite phase, a PYN–PT thin film was synthesized on a $PbTiO_3$ seed layer. The $PbTiO_3$ seed layer was prepared on substrates using 0.1 M $PbTiO_3$ precursor solution. The thin layer of the $PbTiO_3$ precursor on a substrate was dried at 150 °C for 5 min and calcined at 400 °C at a rate of 5 °C/min for 1 h in an O_2 flow, and then heat-treated at 600 °C at a rate of 20 °C/min for 30 min in an O_2 flow. Then, the PYN–PT precursor film was coated on the precrystallized seed layer using 0.1 M solution. Moreover, to control the lead atmosphere during the crystallization process, films were heat-treated with a PYN–PT powder bed. As-deposited PYN–PT precursor films were also dried at 150 °C for 5 min and calcined at 400 °C at a rate of 5 °C/min for 1 h in an O_2 flow, and then crystallized at various temperatures at a rate of 20 °C/min for 30 min in an O_2 flow. The thickness of PYN–PT films was adjusted to be approximately 600 nm by repeating the coating/calcining cycle.

PYN–PT precursor powder was prepared by the removal of solvent from the PYN–PT precursor solution to study the crystallographic phases after heat treatment. The precursor powders were heat-treated between 650 and 750 °C in an oxygen flow for 1 h.

The prepared powders and films were characterized by X-ray diffraction (XRD) analysis using Cu Kα radiation with a monochromator. The surface morphology of the thin films was observed using an atomic force microscope (AFM). The electrical properties of films were measured using a Pt top electrode deposited by DC sputtering onto the surface of PYN–PT films followed by annealing at 400 °C for 60 min. The Pt layer of the Pt/TiO_x/SiO_2/Si substrate was used as a bottom electrode. The electrical properties of the films were evaluated using an impedance/gain phase analyzer (SI-1260, Toyo Corp.) and a ferroelectric test system (FCE-1, Toyo Corp.) at room temperature.

3. Results and discussion

3.1. Preparation of perovskite PYN–PT films

In this study, $0.3Pb(Yb_{1/2}Nb_{1/2})O_3$–$0.7PbTiO_3$ (PYN–70PT) composition was selected in the thin film preparation, because this composition has the tetragonal symmetry as reported by Yamamoto et al. [5]. Prior to the fabrication of ferroelectric PYN–PT thin films, the crystallization behavior of PYN–70PT precursor powder was examined. Fig. 1 shows the XRD patterns of PYN–70PT powders crystallized between 650 and 750 °C. Below 700 °C, PYN–70PT precursor powder crystallized in a mixture of perovskite and pyrochlore phases. On the other hand, all peaks of the powder heat-treated at 750 °C were indexed on the basis of the pseudocubic perovskite PYN–PT phase as shown in Fig. 1(c). Thus, PYN–70PT precursor crystallized in the perovskite PYN–PT phase at 750 °C. From the thermal analysis data of the perovskite PYN–70PT powder, the ferroelectric-paraelectric phase transition (Curie) temperature was found to be about 450 °C. This temperature is consistent with that reported for bulk ceramics [5,6].

In the thin film fabrication, the low-temperature crystallization of thin films is important to achieve the high quality films. On the basis of XRD data of crystallized powders, the crystallization of perovskite PYN–70PT below 700 °C was found to be quite difficult. In general, Pb-based relaxor dielectric material is well-known to crystallize easily in the pyrochlore phase. Therefore, $PbTiO_3$ thin layer was decided to be precrystallized on the substrate as a seed layer. The effect of $PbTiO_3$ seed layer on the low-temperature crystallization of MOCVD-derived perovskite PZT thin films was reported by Shimizu et al. [13]. Fig. 2 shows the XRD profiles of PYN–70PT films crystallized at 700 °C without and with the $PbTiO_3$ seed layer. In this case, the crystallization of perovskite $PbTiO_3$ thin film on substrates was confirmed by XRD. From Fig. 2, the formation of undesirable pyrochlore and unknown phases was effectively

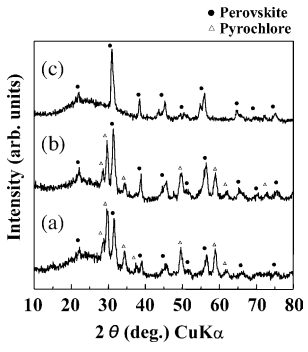

Fig. 1. XRD profiles of $0.3Pb(Yb_{1/2}Nb_{1/2})O_3$–$0.7PbTiO_3$ (PYN–70PT) powders after heat treatment at (a) 650 °C, (b) 700 °C and (c) 750 °C.

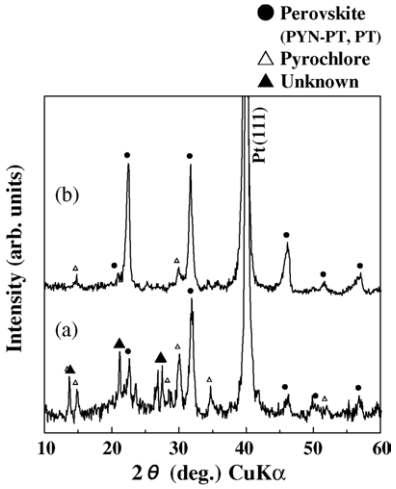

Fig. 2. XRD profiles of PYN–70PT thin films prepared at 700 °C on $Pt/TiO_x/SiO_2/Si$ substrates (a) without and (b) with $PbTiO_3$ seed layer.

suppressed by inserting $PbTiO_3$ seed layer between PYN–PT film and substrate. The nucleation of the perovskite PYN–PT is considered to be assisted by the $PbTiO_3$ seed layer on $Pt/TiO_x/SiO_2/Si$ substrates.

Fig. 3 shows the XRD patterns of PYN–70PT films crystallized between 650 and 750 °C on $Pt/TiO_x/SiO_2/Si$ substrates with $PbTiO_3$ seed layer. Although a little amount of pyrochlore phase was detected, perovskite PYN–PT films were synthesized at 650 °C. This crystallization temperature is about 100 °C lower than that of PYN–PT precursor powders shown in Fig. 1. This result is advantageous for practical applications, because the designed structure in silicon semiconductor devices is often seriously damaged during the heating process.

3.2. Surface morphology of PYN–PT thin films

Fig. 4 shows the AFM images of PYN–70PT thin films synthesized on $Pt/TiO_x/SiO_2/Si$ substrates with $PbTiO_3$ seed

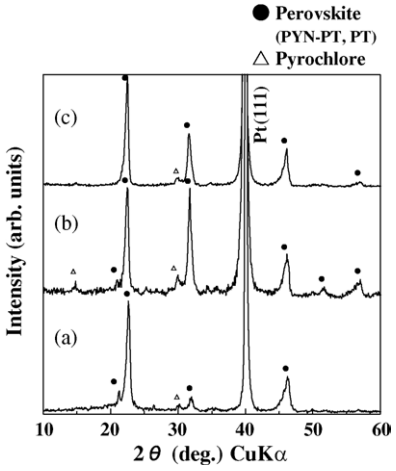

Fig. 3. XRD profiles of PYN–70PT thin films prepared at (a) 650 °C, (b) 700 °C and (c) 750 °C on $Pt/TiO_x/SiO_2/Si$ substrates with $PbTiO_3$ seed layer.

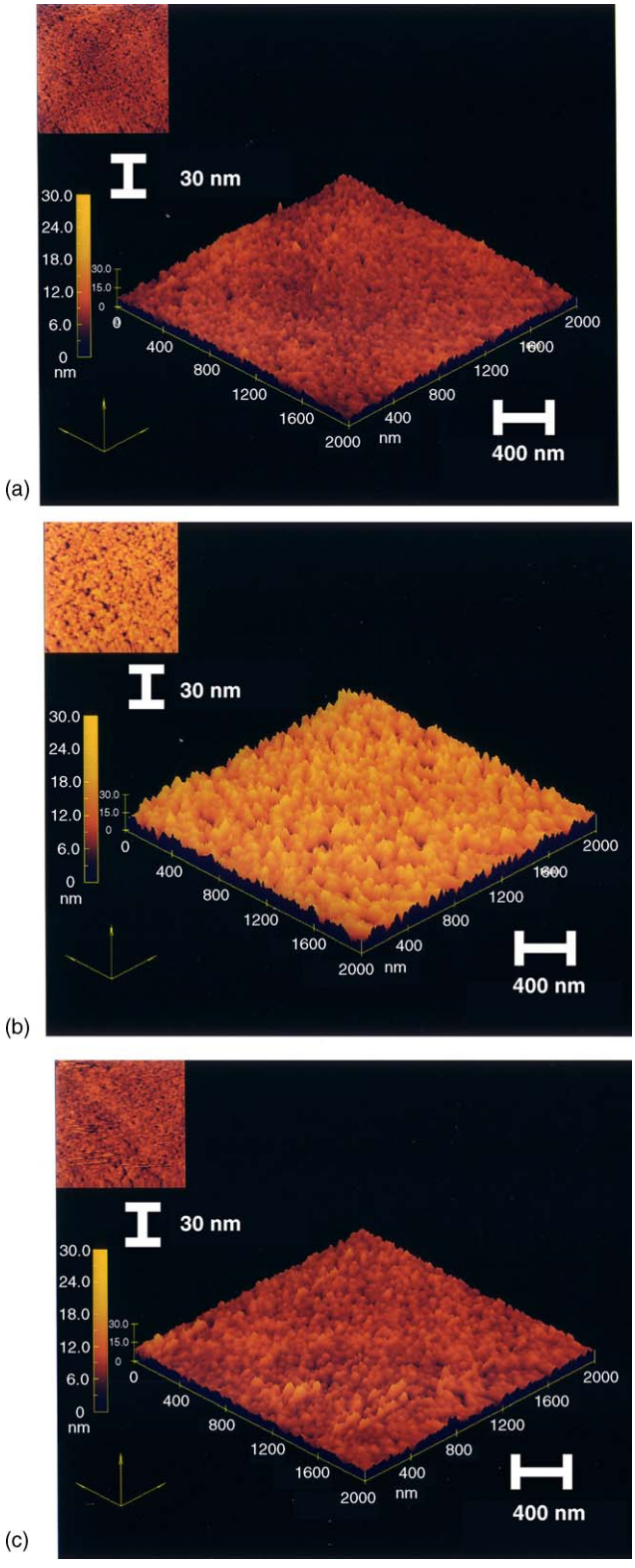

Fig. 4. AFM images of PYN–70PT thin films prepared at (a) 650 °C, (b) 700 °C and (c) 750 °C on $Pt/TiO_x/SiO_2/Si$ substrates with $PbTiO_3$ seed layer.

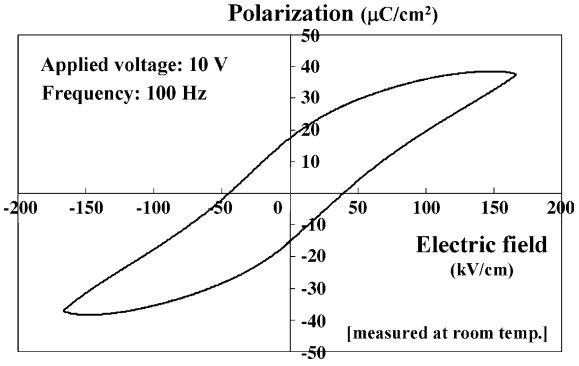

Fig. 5. *P–E* hysteresis loops of PYN–70PT thin films prepared at 700 °C on $Pt/TiO_x/SiO_2/Si$ substrates with without $PbTiO_3$ seed layer.

layer between 650 and 750 °C. It revealed from Fig. 4 that synthesized PYN–70PT thin films had homogeneous and smooth surfaces. The grain size of PYN–PT thin films increased approximately from 50 to 100 nm with raising processing temperature. The mean roughness of the films was found to be about 10 nm regardless of the crystallization temperature. In addition, SEM observation showed that these films had a uniform thickness, with no voids and cracks, which enabled the characterization of dielectric and ferroelectric properties.

3.3. Electrical properties of PYN–PT thin films

P–E hysteresis was measured for the PYN–70PT thin films on $PbTiO_3/Pt/TiO_x/SiO_2/Si$ crystallized at 700 °C. Fig. 5 shows a *P–E* hysteresis loop of PYN–70PT thin film measured at room temperature. The thickness of the film was approximately 600 nm after 10 cycles coating/calcining (including 1 cycle for seed layer) confirmed by SEM observation. This thin film showed a typical ferroelectric *P–E* hysteresis loop at an applied voltage of 10 V. The PYN–70PT thin film exhibited a P_r value of 17.2 μC/cm^2 and E_c of 40 kV/cm. The P_r value was not sufficient as a relaxor-$PbTiO_3$ material. This is due to the residual pyrochlore phase as shown in Fig. 3. The restraint of the formation of pyrochlore and the oriented growth of the films using substrates with good crystallographic matching to PYN–PT are required for the improvement of ferroelectric properties.

Table 1 summarizes the dielectric properties of PYN–70PT thin films prepared between 650 and 750 °C. The PYN–PT thin films exhibited ε_r values of 1100–1500, which depended upon the measured frequency. This behavior of dielectric properties is similar to those of the relaxor dielectrics. The ε_r values increased with raising the crystallization temperature. Although the values of dielectric loss were less than 6%, the ε_r values were lower than those of bulk PYN–PT ceramics [5,6]. Further investigation of the optimization of synthesis conditions and the preparation of highly oriented films using MgO(1 0 0)-based substrates are now in progress.

Table 1
Dielectric properties of synthesized PYN–70PT films (with PT seed layer) at room temperature

Crystallization temperature (°C)	Dielectric constant			Dielectric loss		
	1 kHz	10 kHz	100 kHz	1 kHz	10 kHz	100 kHz
650	1230	1190	1150	0.02	0.02	0.05
700	1340	1280	1230	0.03	0.03	0.05
750	1510	1440	1370	0.03	0.04	0.06

4. Conclusions

Crack-free ferroelectric PYN–70PT thin films were successfully synthesized by a chemical route. Homogeneous and stable PYN–PT precursor solutions were prepared by controlling the reaction of starting metal-organic compounds in 2-methoxyethanol. Perovskite PYN–70PT films were crystallized on $Pt/TiO_x/SiO_2/Si$ substrates above 650 °C using a $PbTiO_3$ seed layer. Furthermore, the PYN–70PT thin films revealed homogeneous and smooth surfaces. PYN–70PT thin film showed the properties of ferroelectrics with a P_r value of 17.2 μC/cm^2 and E_c of 40 kV/cm at 10 V and showed the characteristic behavior of relaxor dielectrics.

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