Dense and crack-free lead zinc niobate–lead zirconate titanate (PZN–PZT) films were deposited on silicon and glass substrates by spin coating using a sol containing propanediol and polyvinylpyrrolidone. Single-layer PZN–PZT films as thick as 0.80 μm were deposited by a single spin coating with successive heat treatments at 250°C and 700°C. After heat treatment, the films were dense, crack free, and optically transparent. In addition, the crystallographic orientation of the thick film was controllable by adjusting the heat-treatment conditions. The ferroelectric properties of the (111)-oriented film were superior to those of the (100)-oriented film. On the other hand, the piezoelectric and dielectric properties of the (100)-oriented film were better than those of the (111)-oriented film. The piezoelectric coefficients \(d_{33}\) of the PZN–PZT films of 4.0-μm-thickness were 192 and 110 pC/N for the (100)- and (111)-oriented films, respectively.

I. Introduction

Lead zirconate titanate (Pb(Zr,Ti)O\(_3\), PZT) solid solution is a well-known and widely used piezoelectric material. A PZT film with a thickness greater than the submicrometer level is one of the most essential requirements in piezoelectric actuators, because the displacement is proportional to the film thickness.\(^1\) Conventional repetitive coating with successive heat treatments using low viscosity sols is a common approach to achieve dense and crack-free films with a thickness greater than the submicron range.\(^2\) However, this process is time consuming and not very attractive for industrial applications. Attempts have been made to prepare crack-free and thick films from a more viscous or highly concentrated sol. Tu and Milne\(^3\) prepared crack-free single-layered PZT thick films using a sol containing 1,3-propanediol (HO(CH\(_2\)\(_3\))OH) as the solvent. They successfully used a high concentration sol (~1.6 M) for the deposition of a 1 μm thick single-layered film; however, their final solution was unstable in air. Kozuka and Takenaka\(^4\) prepared crack-free PZT films of up to 1.6 μm in thickness from a sol containing polyvinylpyrrolidone (PVP), which acted as a viscosity-adjustment and stress-reducing agent. However, the film was rather porous, and exhibited relatively poor ferroelectric properties. Takenaka and Kozuka\(^5\) also reported that when lead nitrate was used as a precursor for the PVP-containing system instead of lead acetate trihydrate, the film was easily densified without any pores being produced. The film fabricated by this method was 0.75 μm thick and showed good optical transparency. However, the solubility of lead nitrate in methoxyethanol is quite limited.\(^6\) Therefore, the PZT concentration of the stock solution was low (~0.35 M), and in order to fabricate a thicker film, they had to deposit the sol by spin coating at a low spin rate (300 rpm), which led to other problems, such as uneven thickness. Recently, a 1-μm-thick PZT film was fabricated by a double spin-coating process at 1300 rpm using a similar system, with PVP as the additive.\(^7\) The film showed strong textures, either (100) or (111), depending on heat-treatment conditions, and fairly good piezoelectric and ferroelectric characteristics.

The lead zinc niobate-modified lead zirconate titanate solid solution system \((0.2\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.8\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3)\) (PZN–PZT) showed enhanced ferroelectric and piezoelectric properties compared with the PZT material.\(^8\) In this study, highly dense 0.80 μm thick PZN–PZT films were fabricated by a single coating using 1,3-propanediol as a solvent and PVP as a viscosity-adjustment additive. As the lead source, lead acetate was used instead of lead nitrate to increase the solubility limit. Thick films up to approximately 10 μm in thickness were fabricated using the multi-coating method. The dielectric, ferroelectric, and piezoelectric properties of the PZN–PZT thick films were characterized.
Glass, Seoul, Korea) to measure the optical transmittance. All observations except for the optical transmittance were carried out using films deposited on a Pt/Ti/SiO\textsubscript{2}/Si substrate. The deposited film was pyrolyzed at 200°–450° C for 10 min on a hot plate. The film was then annealed at 700° C for 10 min at a heating rate of approximately 100° C/min using a vertical tube furnace.

The phases and orientation of the PZN–PZT films were identified by X-ray diffraction (XRD, M18XHF-SRA, Mac Science, Yokohama, Japan). The microstructures of the films were observed using a field-emission scanning electron microscope (FE-SEM, JSM-6330F, JEOL, Tokyo, Japan). The optical transmittance of the films in the visible range was measured using a UV–VIS spectrophotometer (Model 50, Cary Instruments, Monrovia, CA).

A Pt top electrode with a diameter of 0.4 mm was deposited on the film in order to measure the electrical properties. The dielectric properties were measured at 1–100 kHz using an impedance meter (HP 4194A, Hewlett-Packard, Palo Alto, CA), and polarization hysteresis loops were obtained with a standardized ferroelectric test system (TF-2000, AixACT Technologies, Aachen, Germany) using a triangular wave at a frequency of 100 Hz. The effective piezoelectric coefficient was estimated by the strain-monitoring pneumatic loading method,\textsuperscript{9} with the film being poled at a field strength of 150 kV/cm for 100 s.

### III. Results and Discussion

Figure 1 shows the SEM microstructures of the PZN–PZT films deposited on the Pt/Ti/SiO\textsubscript{2}/Si substrate with different diol contents, pyrolyzed at 250° C, and annealed at 700° C. The molar ratio of Pb: diol was varied from 1:0 (0 diol) to 1:20 (20 diol). The PVP content was fixed at a molar ratio of 0.57 with respect to lead acetate. Without the diol, the film showed a porous microstructure, in which the ~0.3 \textmu m grains were agglomerated. As the diol concentration increased, the density of the film increased dramatically. The 10 diol film showed the highest density, and any further increase in the diol concentration deteriorated the surface smoothness of the film, due to the organic residues remaining after the pyrolysis. PVP is known to inhibit the condensation reaction by hybridization with the metalloxane polymers via strong hydrogen bonding, and to promote the structural relaxation in the films.\textsuperscript{10} Diols are known to form highly polymeric species by intermolecular association reactions with alkoxides.\textsuperscript{11} In this study, lead acetate trihydrate was used as the lead precursor, diol as the solvent, and PVP as the viscosity-adjustment agent. From these combinations, viscous and concentrated stock solutions were obtained, which were very stable in air.

Figure 2 shows the phase development of the PZN–PZT films with different diol concentrations. All the films were pyrolyzed at 250° C for 10 min and annealed at 700° C for 10 min. The films without the diol (0 diol) showed a random orientation, where the (110) peak was the most intense. On the other hand, the PZN–PZT film deposited using sols containing diol (≥10 diol) had a (100) and (111) mixed orientation. Generally, the (100) and (111) texture is developed by heterogeneous nucleation at the PbO and Pb\textsubscript{5–7}Pt intermediate phases, respectively.\textsuperscript{12} For the film without the diol, the growth of the film in a specific orientation was inhibited as a result of the high porosity. However, films with the diol are dense enough, so that (100)- and (111)-oriented nuclei were formed at the interface and grew throughout the entire film.

Figure 3 shows the microstructure of the PZN–PZT films deposited using the solution containing 10 diol and annealed at 700° C for 10 min, at different pyrolysis temperatures. The density of the films was strongly dependent on the pyrolysis temperature. Nanosized pores were observed in all the films, which are deemed to have had beneficial effects on the relaxation of the stress during the annealing process. The film pyrolyzed at 200°C (Fig. 3(a)) showed nanosized somewhat isolated pores. The film

![Fig. 1](image_url)  
**Fig. 1.** Scanning electron microscope micrograph of the lead zinc niobate–lead zirconate titanate (0.2Pb(Zn\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}–0.8Pb(Zr\textsubscript{Ti\textsubscript{1–y}}O\textsubscript{3}) films with different diol concentrations; (a) 0 diol, (b) 5 diol, (c) 10 diol, and (d) 20 diol.
Gold viewed at 250°C showed the highest density, as shown in Fig. 3(b). The films pyrolyzed at 350°C and 450°C (Figs. 3(c) and 3(d), respectively) showed relatively large amounts of connected pores, which might be a result of diol evaporation. Those films that were pyrolyzed at ≥ 350°C and were not annealed showed a black color, due to the partially decomposed organics that remained within them. On the other hand, the films pyrolyzed at ≤ 250°C were transparent, and their color immediately changed to black and became transparent again during annealing. From these results, it was estimated that the fast decomposition of the organics during annealing is most favorable for the densification of the PZN–PZT films.

Figure 4(a) shows the XRD patterns of the PZN–PZT films deposited using the solution containing 10 diol and annealed at 700°C for 10 min, with different pyrolysis temperatures. The film pyrolyzed at 250°C showed strong (100) and (111) peaks, and had a weak (110) peak. On the other hand, the films heat-treated at temperatures ≥ 350°C showed a random orientation, which corresponds to the decrease in the film density. To observe the effect of the pyrolysis temperature on the crystallographic orientation, the films were pyrolyzed in the range of 200–300°C with increments of 20°C, followed by annealing at 700°C for 10 min. The XRD patterns of the films annealed at 700°C for 10 min are shown in Fig. 4(b). These XRD patterns show that the (111) orientation is dominant up to 240°C. However, when the pyrolysis temperature was increased to 280°C, the resulting film was mainly oriented in the (100) orientation. The XRD peak intensity ratio \( R_{hkI} = I_{hkI}/(I_{100} + I_{110} + I_{111}) \) was calculated, where \( I_{hkI} \) represents the intensity of the XRD \((hkI)\) peak, and the results are shown in Fig. 4(c). The film pyrolyzed at 240°C had the highest (111) orientation, while the film pyrolyzed at 280°C had the highest (100) orientation. The orientation of the PZT film is reported to be affected by the formation of an intermediate phase such as PbO [001] microcrystals, the Pb5–7Pt intermetallic phase, the stability of the pyrochlore phase, and the residual organic content.12–14 They explained that the orientation of PZT is sensitively changed by these intermediate phases (PbO, Pb5–7Pt, and pyrochlore phases), and their formation mechanisms are strongly dependent on the pyrolysis temperature. In any case, controlling the nucleation mechanism and growth kinetics is important for the development of an oriented film. The PZN–PZT film prepared in this study has a sufficiently high density, and the growth of the nuclei formed at the interface of the film and substrate is not inhibited by the voids. Therefore, the orientation of the film can be adjusted by controlling the nucleation at the interface by varying the heat-treatment schedules.

Fig. 2. X-ray diffraction patterns of the films pyrolyzed at 250°C and annealed at 700°C, with different diol concentrations.

Fig. 3. Scanning electron microscope micrograph of the films deposited using the solution containing 10 diol and annealed at 700°C for 10 min, with different pyrolysis temperatures. (a) 200°C, (b) 250°C, (c) 350°C, and (d) 450°C.
Figure 5(a) shows a cross-sectional view of the PZN–PZT film with a 1:10 ratio of diol and pyrolyzed at 250°C followed by annealing at 700°C. The thickness of the film was about 0.80 μm. The film had a columnar structure with nanosized pores. A multi-layered thick film was deposited by repetitive coating.

Figure 5(b) shows a cross-section view of the approximately 10 μm thick films deposited by applying 15 coatings. This thick film also showed a highly textured columnar structure. These micrographs suggest that the current procedure is suitable for the deposition of high-quality 1–10 μm thick films.

The optical transmittances of around 0.80 μm thick PZN–PZT films deposited on the ITO coated glass substrate in the visible wavelength range are shown in Fig. 6. The optical transmittance of the ITO/glass substrate without the PZN–PZT film was plotted in the same graph for the purpose of comparison. The spectra showed interference oscillations caused by the structure of the film. The transmittance of the film exhibited a sharp UV absorption edge at approximately 400 nm, which is close to that reported for the bulk transparent lead lanthanum zirconate titanate (PLZT) in the perovskite phase. Figure 6(a) shows the transmittance of the PZN–PZT films deposited using solutions with different diol contents. The film deposited using a solution containing 10 diol showed the highest optical transmittance, while the film deposited using the solution without the diol showed a poor optical transmittance. The transmittances of the annealed PZN–PZT films pyrolyzed at different temperatures are shown in Fig. 6(b). The film pyrolyzed at 250°C showed the highest transmittance. The results suggest that a 1:10 molar ratio of Pb:diol and a pyrolysis temperature of 250°C are the optimum conditions, which is in accordance with the SEM and XRD results.

Figure 7 represents the P–E hysteresis loops of the 0.80 μm thick PZN–PZT films oriented along the (100) and (111) directions. The remanent polarization (P_r) and coercive field (E_c) of the (100)-oriented PZN–PZT film were 16 μC/cm² and 22 kV/cm, respectively, while those of the (111)-oriented film were 21 μC/cm² and 27 kV/cm, respectively. For the rhombohedral composition, the (111)-oriented film exhibited a higher P_r value than the (100)-oriented films, because the spontaneous polar axis is along the [111] direction.

Figure 8 shows the relative dielectric constants of the (100)- and (111)-oriented 0.80 μm thick PZN–PZT films pyrolyzed at 240°C and 280°C and annealed at 700°C, as a function of the frequency. The relative dielectric constant and dielectric loss of
the (100)-oriented PZN–PZT film were 1900 and 0.066, respectively, while those of the (111)-oriented film were 1100 and 0.068, respectively. The relative dielectric constant is known to be higher for the (100)-oriented film than for the (111)-oriented film. These results are in good agreement with the theoretical expectations and also show fairly good values, which are comparable with the results obtained from dense PZT films deposited using a multiple sol–gel-coating process or reactive radio frequency sputtering.

The piezoelectric properties of the PZN–PZT thick films were measured using ~4.0 μm thick PZN–PZT films (deposited six times) deposited by a 1:10 diol solution, and pyrolyzed and annealed at ~250° and 700°C, respectively. Figure 9 shows the $d_{33}$ coefficient of the (100)- and (111)-oriented PZN–PZT films fabricated using a diol-based solution containing PVP. For the purpose of comparison, PZT films with the same thickness were fabricated by the multi-coating method (42 coatings) using the conventional methoxyethanol-based sol–gel method. The $d_{33}$ value has a maximum value when the crystal structure is oriented in a direction 59.4° away from the polarization direction (111), which is very close to the perovskite (100) direction. In our results, the (100)-oriented film has a higher piezoelectric coefficient than the (111)-oriented film, which is in accordance with the theoretical expectation. Furthermore, the PZN–PZT film grown using the modified sol–gel method showed a higher $d_{33}$ value than the PZT film grown using the conventional sol–gel method. An increase in the piezoelectric properties of the PZT system afforded by PZN modification has previously been reported in bulk materials. In addition, the PZN–PZT film consisting of a 0.80 μm thick single layer fabricated using the modified sol–gel method had a larger grain size than the PZT film comprising a 0.10 μm thick single layer fabricated using the conventional sol–gel method.
IV. Summary and Conclusions

Thick PZN–PZT films were deposited on silicon and glass substrates using the sol–gel method with a lead acetate trihydrate–zirconium n-propoxide–titanium n-propoxide solution containing 1,3-propanediol and PVP. The films deposited using the solution containing a 1:10 Pb/diol molar ratio and heat-treated at 250°C and 700°C were dense, crack free, and optically highly transparent. The orientation of the thick film could be controlled by adjusting the heat-treatment conditions. The remanent polarization, coercive field, and relative dielectric constant of the 0.80 μm thick (100)-oriented PZN–PZT film were 16 μC/cm², 22 kV/cm, and ~1900, respectively, while those of the (111)-oriented film were 21 μC/cm², 27 kV/cm, and ~1100, respectively. The piezoelectric d33 coefficient of the ~4.0 μm thick (100)-oriented and (111)-oriented PZN–PZT films were 192 and 110 pC/N, respectively.

References


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