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Preparation of Ferroelectric $Pb(Zr_{0.52}\ Ti_{0.48})O_3$ Thin Films by Sol-Gel Processing

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Abstract–Ferroelectric $Pb(Zr_{0.52}\ Ti_{0.48})O_3$ thin films were prepared by sol-gel processing on the $Pt/Ti/SiO_2/Si(100)$ substrates. Effects of the concentration (0.2-0.8 M) of the starting solution (Pb/Zr/Ti=1.1/0.52/0.48) and the sintering temperature (500-700 °C) on crystallinity, microstructure and electrical properties of PZT thin films were investigated. For the thin film prepared at 0.4 M starting solution, the highest crystallinity appeared at a sintering temperature of 650 °C. The average grain size of the PZT thin films was about 0.17 μm. The film thickness was about 0.2 μm. The relative dielectric constant and the dissipation factor of the film measured at 1 kHz were about 750 and 4.3%, respectively. The remnant polarization (Pr) and coercive field (Ec) of the film measured at the applied voltage of 5 V were about 49 $\mu C/cm^2$ and 134 kV/cm, respectively.

Key words: Ferroelectric, Thin Films, Sol-Gel Processing, PZT, Perovskite Phase, Relative Dielectric Constant, Dissipation Factor

INTRODUCTION

Recently, $Pb(Zr, Ti)O_3$ thin films have been potential candidates for use in nonvolatile memories (ferroelectric random access memory, FRAM), sensors, infrared detectors and surface acoustic wave (SAW) because of their excellent electrical and optical properties [Haerting, 1991; Takayama and Tomita, 1989]. Parameters for preparing PZT thin films have been studied since the properties of thin films depend on factors such as ratios of Zr and Ti, sintering temperature [Lee et al., 1999] and film thickness [Amanuma et al., 1993]. Various methods for preparation of PZT thin films have been reported, such as chemical vapor deposition (CVD) [Chung and Kim, 1997; Jin et al., 1998; Kim et al., 1996], sputtering [Krupanidhi et al., 1983; Sreenivas and Sayer, 1988], hydrothermal synthesis [Seo and Kong, 2000] and sol-gel processing [Klee et al., 1992]. Compared to other techniques, sol-gel processing has simpler composition control, better thin-film homogeneity, lower synthesis temperature, lower cost and easier fabrication of large area [Meidong et al., 1995]. In particular, the composition with Zr/Ti= 52/48 lies at the morphotropic phase boundary (MPB), which corresponds to a transition from tetragonal to rhombohedral structure. At this phase boundary, most of the properties such as dielectric constant, piezoelectric coefficient and others show their maximum values [Iijima et al., 1991; Caruso et al., 1999]. It is also very important to control the process parameters, such as the concentration of starting solution and the sintering temperature in order for the thin films to be implemented through an industrial sol-gel processing.

In this study, ferroelectric $Pb(Zr_{0.52}\ Ti_{0.48})O_3$ thin films were prepared from sol-gel processing by spin-coating a PZT starting solution on $Pt/Ti/SiO_2/Si(100)$ substrates. In order to maintain the crystal structure of the PZT thin films at the morphotropic phase boundary, the molar ratio of Pb/Zr/Ti in the starting solution was fixed as 1.1/0.52/0.48. The effects of process parameters, such as the concentration of starting solution and the sintering temperature, on crystallinity, microstructure and electrical property of PZT thin films for DRAM or FRAM applications were investigated.

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EXPERIMENTAL

1. Preparation of the Starting Solution

In preparing the starting solution (Pb/Zr/Ti=1.1/0.52/0.48), we dissolved lead acetate trihydrate, $Pb(CH_3COO)_2{\cdot}3H_2O$ (99.5%, Junsei), titanium iso-propoxide, $Ti(OCH(CH_3)_2)_4$ (98%, Junsei) and zirconium n-butoxide, $Zr(O(CH_2)_3CH_3)_4$ (80%, Aldrich) as raw materials in isopropyl alcohol. 0.05 M HNO_3 (10 ml) was added to control the hydrolysis-condensation rates and the structure of the condensed product [Brinker and Scherer, 1990]. DEA (diethanolamine, 5 ml) was also added to the feedstock solution (150 ml) in order to improve clarity, stability and homogeneity. A further amount of 10 mol% lead acetate trihydrate was added to compensate for the PbO losses during sintering of the thin films. The feedstock solution was aged for 24 hours at room temperature. The concentrations of the starting solution were 0.2, 0.4, 0.6 and 0.8 M.

2. Preparation of PZT Thin Films

Oxidized silicon wafer was used as a substrate in the experiment. The platinum bottom electrode (170 nm) with a titanium adhesive layer (50 nm) was deposited on this substrate. PZT thin films were prepared by spin coating at the speed of 3,000 rpm for 30 seconds and dried at about 150 °C for 1 minute, then calcined at 400 °C (a heating rate of 10 °C/min) for 5 minutes. The above processing was repeated three times in order to obtain an appropriate film-thickness (0.2-0.3 μm) and compactness. The coated films were sintered in the range of 500-700 °C for 20 minutes in an air environment, and cooled down to room temperature in the furnace. The flow diagram for PZT thin film preparation is shown in Fig. 1.

3. Measurement

A differential thermal and thermogravimetric analyzer, DT-TGA

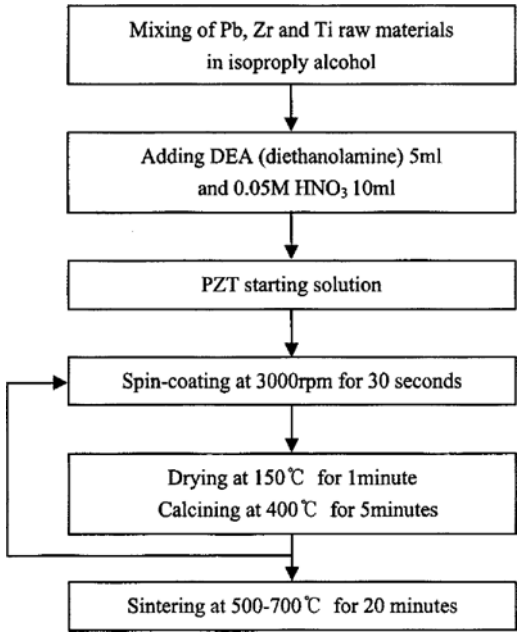

Fig. 1. The flow diagram for PZT thin films preparation.

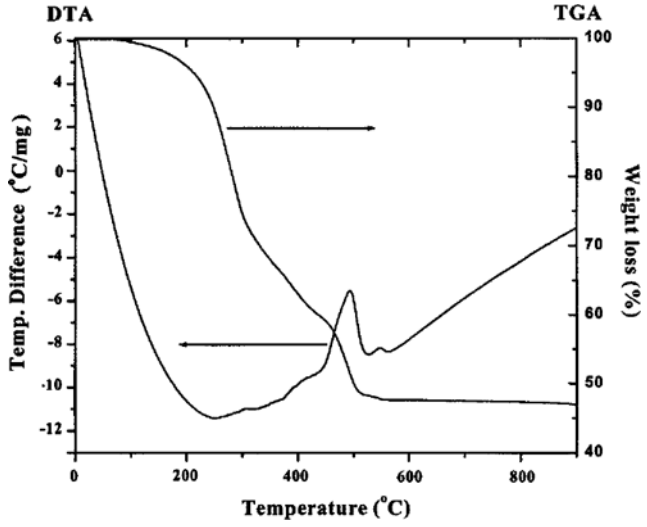

Fig. 2. The DT-TGA curves of the PZT gel dried at 150 °C for 2 hours. The gel was prepared using 0.4M starting solution (Pb/Zr/Ti=1.1/0.52/0.48).

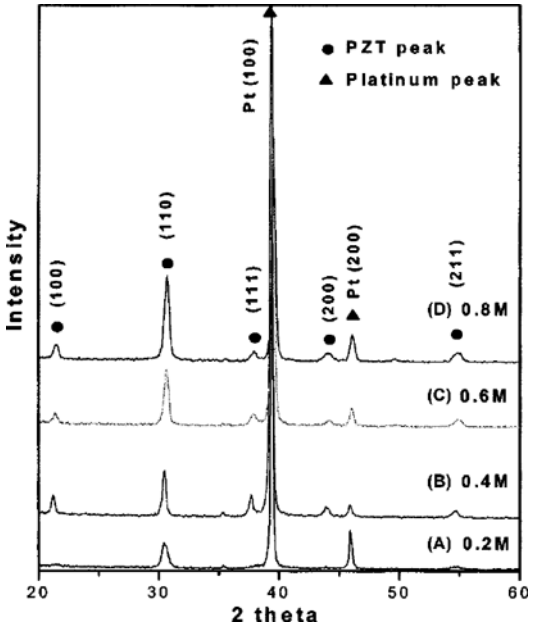

Fig. 3. XRD patterns of PZT thin films when the concentrations of the starting solution (Pb/Zr/Ti=1.1/0.52/0.48) were (A) 0.2 M, (B) 0.4 M and (C) 0.8 M. The films were prepared by three times of a spin coating (3,000 rpm, 30 seconds), and sintered at 650 °C for 20 minutes.

(Toledś, Mettler) was used in order to investigate the thermal characteristics of PZT gel. The crystalline structure of the PZT thin films was analyzed with an X-ray diffractometer (XRD: M03XHF, MAC Science) using a monochromatic Cu K_α radiation, 40 kV, 30 mA in the range of 20-60°. The microstructure of the thin film was observed by using a scanning electron microscope (SEM: JSM-840A, JEOL). The thickness of the thin film was measured with a mechanical stylus profilometer (Tensor, P-10). To measure the electrical properties of thin films, Pt-top electrode (ϕ=0.15 mm) was used. The relative dielectric constant and the dissipation factor were measured with an impedance analyzer (HP-4194A). The remnant polarization (Pr) and coercive field (Ec) were determined from P-E hysteresis loops measured with a ferroelectric tester (RT-66A, Radiant Technology).

RESULTS AND DISCUSSION

1. Thermal Analyses of the Starting Solution

The PZT gel dried at 150 °C was heated from room temperature to 800 °C at a heating rate of 5 °C/min in an air environment.

Fig. 2 shows the DT-TGA curves of the PZT gel dried at 150 °C for 2 hours. The gel was prepared by using 0.4 M starting solution (Pb/Zr/Ti=1.1/0.52/0.48). A weight loss appeared near 200 °C due to the decomposition of the residual water compounds in the PZT gel. A great weight loss appeared near 500 °C due to the decomposition of organic compounds. The exothermic peak appeared near 550 °C, which illustrates the crystallization of the PZT grain. The synthesis temperature for sol-gel processing was found to be lower than that of traditional powder processing (over 850 °C). This is because the PZT materials were uniformly mixed in the solution and contacted each other in molecule orders. The diffusion distance among atoms was relatively short and the high activity allowed the PZT to be quickly crystallized. Consequently, the crystallization temperature was lowered. The calcination and sintering temperatures in the experiment were chosen by thermal analysis as 400 °C and 500-700 °C, respectively.

2. Effects of the Concentration of the Starting Solution

Fig. 3 shows XRD patterns of PZT thin films when the concentrations of the starting solution (Pb/Zr/Ti=1.1/0.52/0.48) were (A) 0.2 M, (B) 0.4 M, (C) 0.6 M and (D) 0.8 M. The films were sintered at 650 °C for 20 minutes. The PZT(111) and (200) peaks of XRD patterns were not obviously apparent when the concentration of the starting solution was 0.2 M. However, the PZT crystalline peaks of the perovskite phase appeared (2 theta=22°, 31°, 38°, 45°

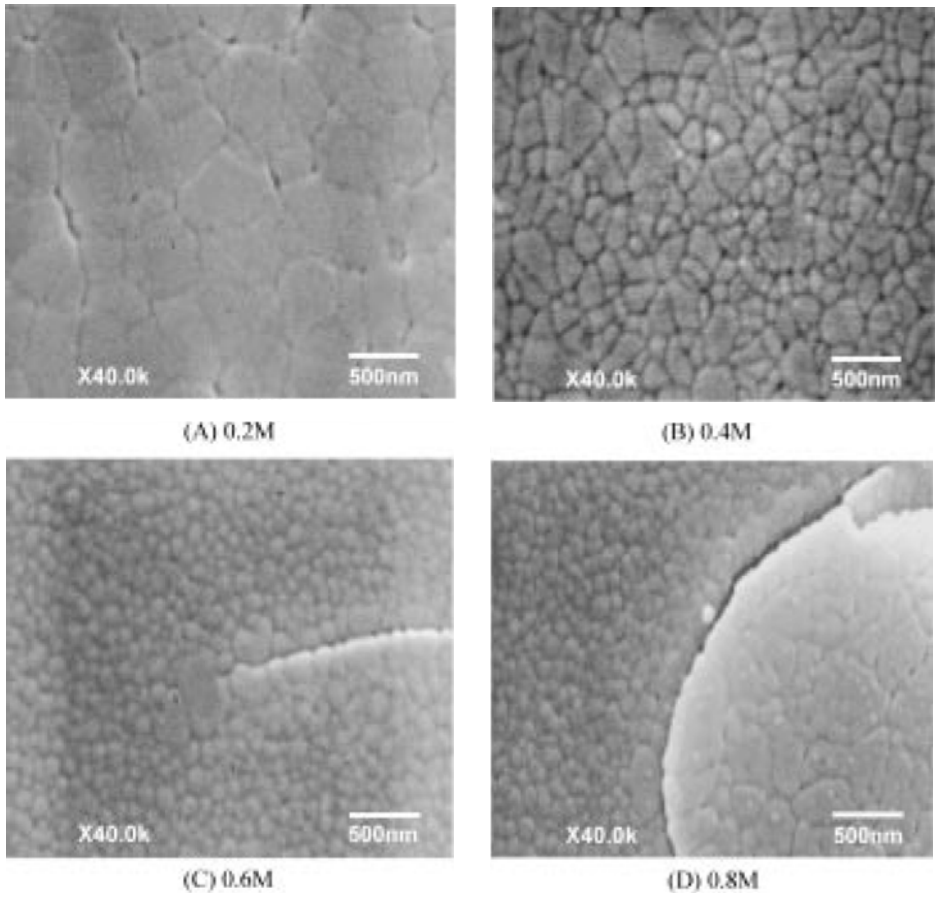

Fig. 4. SEM micrographs of the PZT thin films mentioned in Fig. 3.

and 55°) in the case of thin films prepared by using 0.4 M starting solution. The highest peak of diffraction intensity was obtained when the concentration of the starting solution was 0.8 M. Fig. 4 shows SEM micrographs of the PZT thin films mentioned in Fig. 3. Pores and uncrystallized grain boundaries appeared at (A) 0.2 M. Hundred nanometer-sized grains of a compact and crack-free structure were obtained at (B) 0.4 M, but a crack appeared on the film surface at (C) 0.6 M. Peeling on the film surface was found at (D) 0.8 M. Table 1 shows the correlation of film thickness and the viscosity with the concentration of the starting solution. The thickness of PZT thin film prepared by using 0.4 M starting solution was about 0.2 μm, and viscosity of that starting solution was about 3.2 cP (centipoise, 10^{-2} g/cm·s). From the above results we can say that as the

Table 1. The correlation of film thickness and viscosity with the concentration of the starting solution (Pb/Zr/Ti=1.1/0.52/0.48). The films were prepared by three times of a spin coating (3,000 rpm, 30 seconds), and sintered at 650 °C for 20 minutes

The concentration of starting solution (M)	The viscosity of starting solution (cP)	Film thickness (μm)
0.2	2.7	0.10
0.4	3.2	0.20
0.6	3.8	0.25
0.8	4.5	0.30

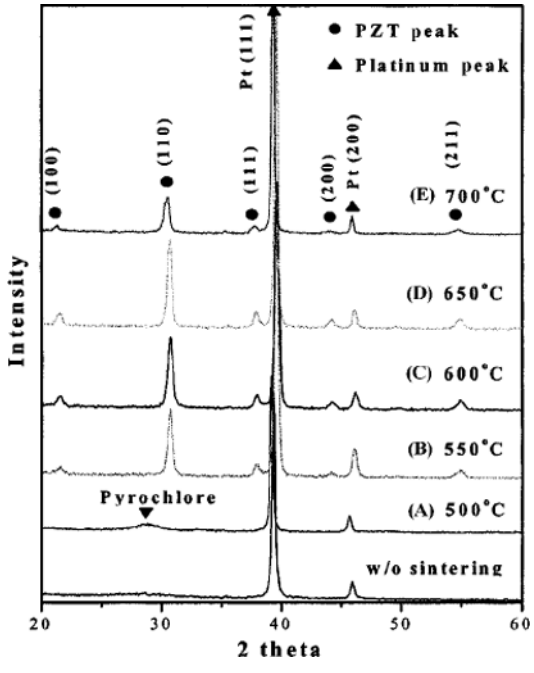

Fig. 5. XRD patterns of thin films sintered at (A) 500 °C, (B) 550 °C, (C) 600 °C, (D) 650 °C and (E) 700 °C for 20 minutes when the concentration of the starting solution (Pb/Zr/Ti=1.1/0.52/0.48) was 0.4 M. The films were prepared by three times of a spin coating (3,000 rpm, 30 seconds).

concentration of the starting solution increased, causing an increase in the viscosity of that solution, adhesion of thin film on the substrate became incomplete due to an increase of thermal stress between film and bottom electrode during the sintering process. Incomplete adhesion of thin film on the substrate causes a propagation of cracks or peelings. The viscosity and surface tension of the solution can be adjusted by controlling the concentration of the starting solution [Yi et al., 1988]. Therefore, the optimum concentration and viscosity of the starting solution should be used for the best thin film preparation in the sol-gel processing. From the results shown in Figs. 3, 4 and Table 1, the optimum concentration of the starting solution (Pb/Zr/Ti=1.1/0.52/0.48) was chosen as 0.4 M, which was used in the following experiments since a crack-free structure could be obtained with that concentration of starting solution.

3. Effects of the Sintering Temperature

Fig. 5 shows XRD patterns of thin films, sintered at (A) 500 °C, (B) 550 °C, (C) 600 °C, (D) 650 °C and (E) 700 °C for 20 minutes when the concentration of starting solution (Pb/Zr/Ti=1.1/0.52/0.48) was 0.4 M. The films were prepared by three times of a spin coating (3,000 rpm, 30 seconds). The thin films were calcined at 400 °C. When the thin film was prepared without sintering, only an amorphous structure appeared. When the thin film was sintered at 500 °C, as shown in Fig. 5(A), a pyrochlore phase, which is stable at low temperature, appeared near 28°. However, the pyrochlore phase disappeared when the film was sintered, while the PZT crystalline peaks of the perovskite phase appeared, as shown in Fig. 5(B). The diffraction intensity of PZT crystalline peaks slightly decreased at the sintering temperature of 700 °C due to volatilization of PbO, as shown in Fig. 5(E).

Fig. 6 shows SEM micrographs of thin films sintered at (A) 600 °C, (B) 650 °C and (C) 700 °C for 20 minutes. Uncrystallized grains and pores appeared at 600 °C, as shown in Fig. 6(A), and disappeared as the sintering temperature increased. At a sintering temperature of 650 °C, as shown in Fig. 6(B), the microstructure of the thin film showed compact grains, the average size of which is about 0.17 μm. Smaller grains of about 20-30 nm appeared at 700 °C, as shown in Fig. 6(C). In general, a typical PZT thin film has a microstructure of a "rosette" [Kim et al., 1997] with micron-sized and non-uniform grains. The rosette structure leads to serious problems in the application of the FRAM device. However, we could not find the rosette structure on the thin films prepared, as shown in the figure. From the results of SEM and XRD analyses, we found degradation of PZT crystallinity at 700 °C. This is due to the partial volatilization of PbO. Volatilization of PbO causes the stoichiometry and structure of the film to fail [Chang and Chen, 1999]. If the sintering temperature increases higher than 700 °C, more volatilization of PbO occurs, which may lead to the failure of PZT crystallinity of the film.

Fig. 7 shows SEM micrographs of the cross-section of the PZT thin film. The film was sintered at 650 °C for 20 minutes. As we can see in the figure, the Pt/Ti and PZT layers were clearly distinguished. The thickness of the PZT layers was about 0.2 μm.

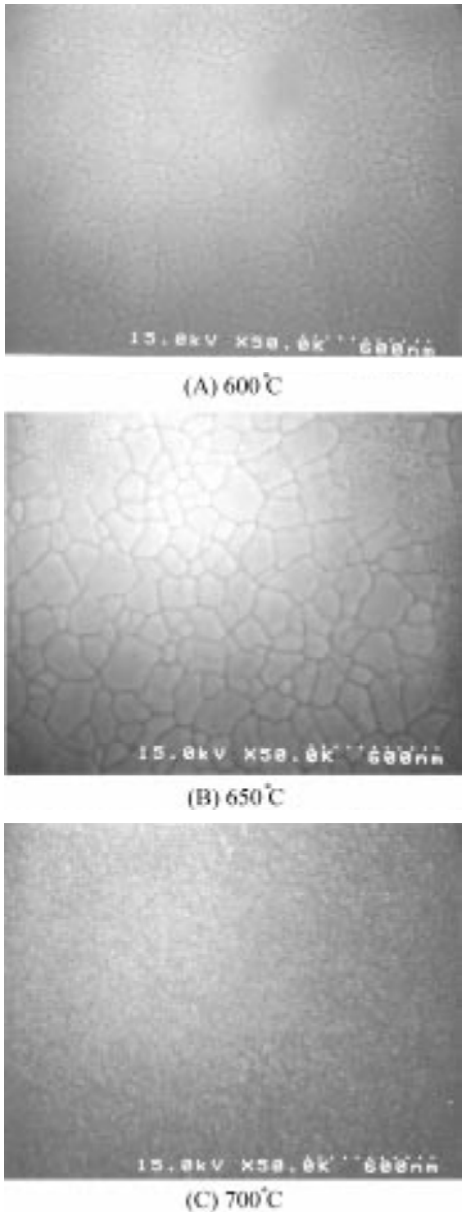

Fig. 6. SEM micrographs of thin films sintered at (A) 600 °C, (B) 650 °C and (C) 700 °C for 20 minutes when the concentration of the starting solution (Pb/Zr/Ti=1.1/0.52/0.48) was 0.4 M. The films were prepared by three times of a spin coating (3,000 rpm, 30 seconds).

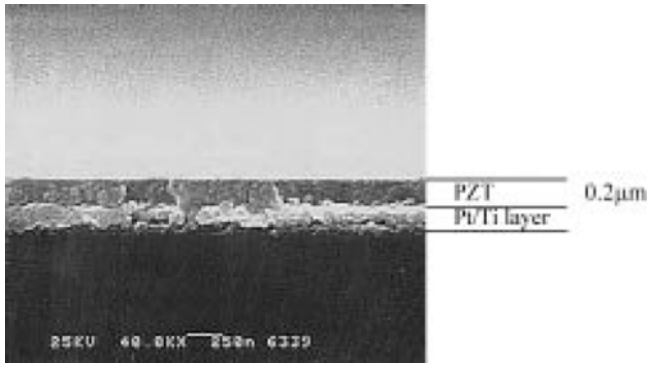

Fig. 7. SEM micrograph of the cross-section of the PZT thin film prepared by three times of spin coating (3,000 rpm, 30 seconds). The film was sintered at 650 °C for 20 minutes. The concentration of the starting solution (Pb/Zr/Ti=1.1/0.52/0.48) was 0.4 M.

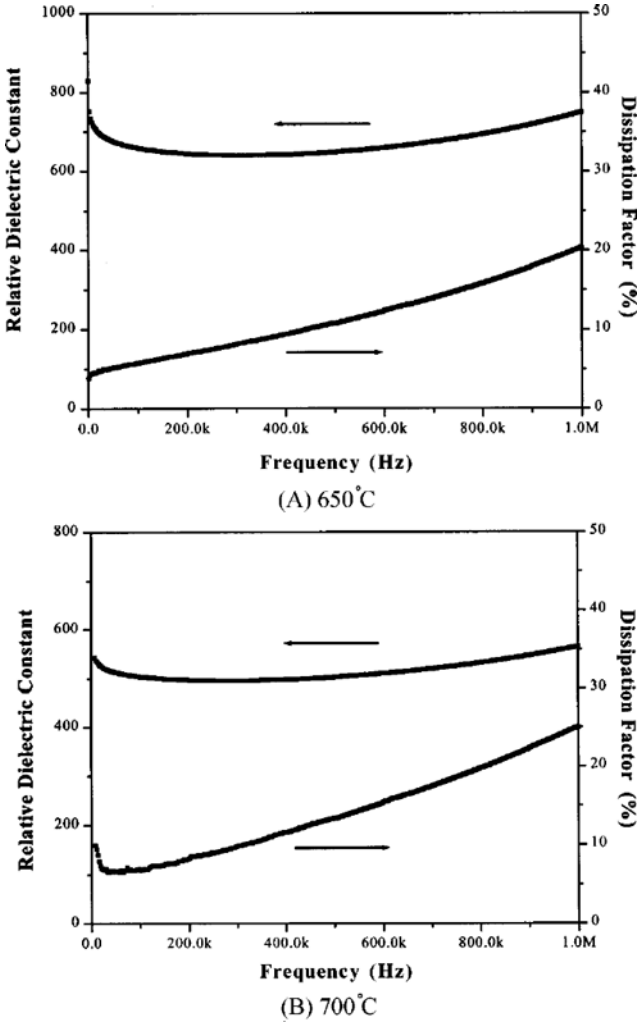

Fig. 8. The relative dielectric constant and dissipation factor of the PZT thin films sintered at (A) 650 °C and (B) 700 °C for 20 minutes. The concentration of the starting solution (Pb/Zr/Ti=1.1/0.52/0.48) was 0.4 M. The films were prepared by three times of a spin coating (3,000 rpm, 30 seconds).

Fig. 8 shows the relative dielectric constant and the dissipation factor of the PZT thin film sintered at (A) 650 °C and (B) 700 °C for 20 minutes. The relative dielectric constant and the dissipation factor measured at 1 kHz were about 750 and 4.3%, and 550 and 6.6%, respectively. P-E hysteresis loops of the above-mentioned PZT thin films measured by a Sawyer-Tower circuit are shown in Fig. 9. The remnant polarization (Pr) and the coercive field (Ec) of the thin films mentioned above were measured. The remnant polarizations (Pr) at the applied voltage of 5 V were about 49 $\mu C/cm^2$ (650 °C) and 38 $\mu C/cm^2$ (700 °C). The coercive fields (Ec) at the same applied voltage were about 134 kV/cm (650 °C) and 72 kV/cm (700 °C). These values are quite greater than the experimental results shown in the references [Seo and Kong, 2000; Jeon and Yoo, 1998]. From these results we can say that the PZT thin film prepared at 650 °C has the appropriate dielectric properties for a good ferroelectric application, despite the asymmetric features in P-E hysteresis loops, which are due to the existence of the contact resistance between the bottom electrode and the thin film.

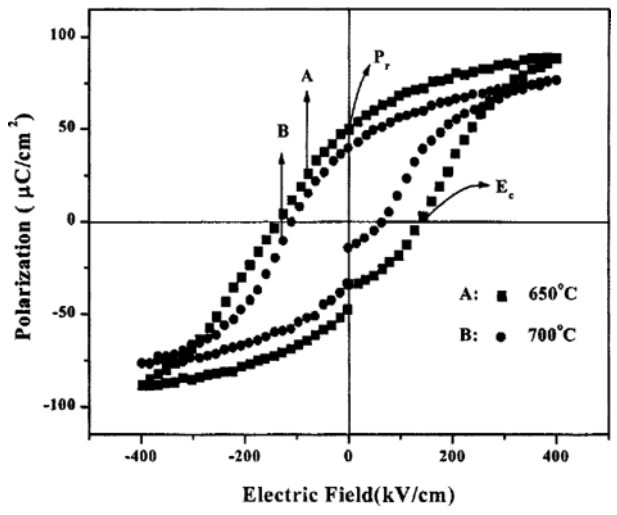

Fig. 9. P-E hysteresis loops of the PZT thin films mentioned in Fig. 8. The applied voltage was 5 V.

CONCLUSION

In this study, a PZT thin film, which has acceptable electrical properties for DRAM or FRAM application, was prepared by sol-gel processing. For the PZT thin film fabricated by using 0.4 M starting solution (Pb/Ti/Zr=1.1/0.52/0.48) and sintered at 650 °C, the microstructure with the perovskite phase was free of cracks and showed compact grains of about 0.17 μm, and film thickness was 0.2 μm. The relative dielectric constant and dissipation factor of the thin film measured at 1 kHz were about 750 and 4.3%, respectively. The remnant polarization (Pr) and coercive field (Ec) measured at the applied voltage of 5 V were about 49 $\mu C/cm^2$ and 134 kV/cm, respectively.

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