Dielectric Properties of PZT(20/80)/PZT(80/20) Heterolayered Thick Films Fabricated by Screen-printing Method

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Ferroelectric PZT heterolayered thick films were fabricated by the alkoxide-based sol-gel method. PZT(20/80) and PZT(80/20) paste were made and alternately screen-printed on the alumina substrates. The coating and drying procedure was repeated 4 times to form the heterolayered thick films. The thickness of the PZT heterolayered thick films was approximately 60 μm. All PZT thick films showed the typical XRD patterns of a polycrystalline rhombohedral structure. And in the PZT thick films sintered at 1100 °C, the pyrochlore phase was observed due to the evaporation of PbO. The relative dielectric constant and the dielectric loss of the PZT thick films sintered at 1050 °C were 445.2 and 1.90 % at 1 kHz, respectively. The remanent polarization and coercive field of the PZT thick films sintered at 1050 °C were 14.15 $\mu C/cm^2$ and 19.13 kV/cm, respectively.

1. INTRODUCTION

ABO_3 perovskite-type lead zirconate titanate $(Pb(Zr,Ti)O_3, PZT)$ material is one of the most important electrical and electronic ceramics materials for use in capacitors of dynamic random access memories (DRAMs), gate materials of ferroelectric RAM (FeRAM), piezoelectric transducers, pyroelectric infrared detectors and non-linear optical devices[1-3]. PZT ceramics, which exhibit a high spontaneous polarization and a high dielectric constant, were widely investigated because of their potentials for low temperature processing and various electrical properties obtained by varying the composition ratio or adding the dopants. Recently, an effective and reliable technology for fabrication of actuators made of piezoelectric thick films is required as a part of the manufacture of micropumps, ultrasonic mixers in micro electro-mechanical systems (MEMS) and micro total analysis system (μ-TAS), micromanipulators for medical applications, ink-jet printer heads, flapper actuators for high-density hard-disk drive, and others, which need large strain and high-speed response[4]. These applica-tions of piezoelectric/electrostrictive materials often require dense and thick micropatterned films with a thickness of more than 10 μm and low process temperature.

The various film preparation methods for PZT family were improved during the development of ferroelectric memory devices, and the thickness of the resultant films were usually less than 1 μm. There are some reports on fabrication of PZT thick films by sol-gel method, screen printing method, sputtering method and hydrothermal synthesis method[5,6]. The screen printing method is especially useful for a high productivity and good cost performance brings the films to the stage of commercial mass production.

Generally, the structural and electrical properties of PZT films depend on the fabrication process, sintering conditions, composition, and dopants. We have already reported on the good electrical properties of PZT heterolayered thin films which they were alternately spin-coated using PZT(20/80) and PZT(80/20) metal alkoxide solutions[7].

In this study, PZT(20/80)/PZT(80/20) heterolayered thick films were prepared by the screen printing

techniques, in which they were alternately screen-printed on the high purity alumina substrates using PZT(20/80) and PZT(80/20) pastes. The objective of the present study is to investigate the structural and dielectric properties of the PZT heterolayered thick films for various transducers and electronic devices applications.

2. EXPERIMENTAL

PZT(20/80) and PZT(80/20) powders with excess Pb-acetate 10 mol% were prepared from Pb acetate trihydrate $(Pb(CH_3CO_2)_2 \cdot 3H_2O)$, Zr propoxide (Zr $(OCH_2CH_2CH_3)_4)$ and Ti iso-propoxide (Ti[OCH $(CH_3)_2]_4$) as the starting materials, and 2-methoxyethanol $(CH_3OCH_2CH_2 OH)$ as the solvent using the sol-gel method[8]. Pb acetate was dissolved in 2-methoxye-thanol, and then the solution was heated for the evaporation of water. After cooling, Zr propoxide and Ti iso-propoxide, dissolved in 2-methoxyethanol, were added to the solution. The mixed solution was refluxed and then 2-methoxyethanol and water were added to the solution for stabilization and hydrolysis, respectively. The powder precursors were dried and calcined at 850 °C for 2 h in a high purity alumina crucible. The calcined powders were ground by using planetary ball milling for 24 h.

The screen-printable pastes were prepared by kneading the ground PZT powder with 30 wt% of organic vehicle (Ferro B75001) in a non-bubbling kneader (NBK-1, Kyoto Electro.). The Pt bottom electrodes were screen-printed on the high purity alumina substrate. The tetragonal PZT(20/80) paste was screen-printed on the substrates to form the first layer. These PZT(20/80) layers were dried, and then rhombohedral PZT(80/20) paste was screen-printed to form the second layer. This procedure was repeated four times. These PZT thick films were sintered at 950-1100 °C for 2 h in PbO atmosphere. The crystalline structure, the microstructures and the composition distribution of the surface were examined using X-ray diffraction (XRD) and scanning electron microscopy SEM-EDS (Philips XL30S FEG), respectively. The upper electrodes were fabricated by screen printing the Ag paste. After poling with a field of 30 kV/cm for 30 min at 120 °C, the dielectric properties of the specimens were measured using an LCR-meter (ANDO 4301) with variation of frequency. Ferroelectric properties were measured using a ferroelectric tester (Radiant, RT-66A).

3. RESULTS AND DISCUSSION

Figure 1 shows the surface Pb, Zr and Ti contents of the PZT thick film with variation of the sintering tem-
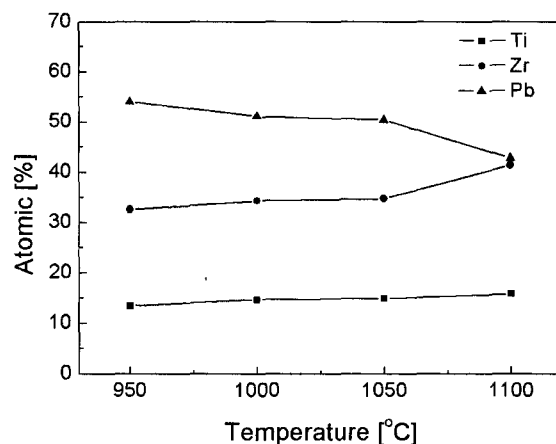

Fig. 1. Dependence of the film surface composition on sintering temperature.

perature. With increase of the sintering temperature from 950 °C to 1100 °C, the Pb concentration in the film slowly decreases. The reason for this is assumed to be that the volatile of PbO increased with increasing the sintering temperature. The high concentration of Pb at 950 °C of sintering temperature is due to excess PbO. The PZT thick films sintered at 1050 °C become close to stoichiometry and the value of Pb/(Zr+Ti) is 1.0161. However, in the PZT films sintered at 1100 °C, the Pb content rapidly decreased due to the evaporation of PbO at excessively high sintering temperature, the value of Pb/(Zr+Ti) is 0.7477. Also, the Zr content increased because of the relative distribution of its high composition ratio.

Figure 2 shows the X-ray diffraction patterns of PZT heterolayered thick films printed on Pt/alumina substrate with variation of sintering temperature. Generally, the XRD peaks of the substrate were not detected in the thick films due to their thickness. However, in this study, the XRD peaks of the Pt electrode (JCPDS No. 040802) were detected. The reason for this is assumed to be that the PZT thick films exhibited a porous microstructure and some large pores, as shown in Fig. 3. All PZT thick films showed the typical XRD patterns of a perovskite polycrystalline structure. But, in the PZT heterolayered thick films sintered at 1100 °C, the pyrochlore phase was observed at around 2 θ = 28 ° and 46 ° due to the evaporation of PbO at high sintering temperature, as shown in Fig. 1. In the PZT heterolayered thin films, the crystalline structure of the upper PZT layers depend strongly on the crystalline phase of the lower PZT layer[9]. But, in the PZT heterolayered thick films fabricated by the screen-printing method, the effect of the lower PZT layers was not observed, because the thickness of the each layer is high. The thickness of the one layer PZT film was approximately 15 μm.
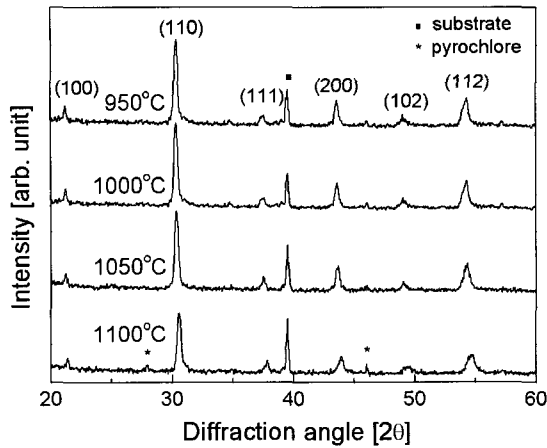
Fig. 2. XRD patterns of the PZT(20/80)/PZT(80/20) heterolayered thick films.

Figure 3 shows the surface and cross-section SEM micro graphs of the PZT heterolayered thick films printed on Pt/alumina substrate for various sintering temperature. The PZT thick films sintered at 950 °C exhibited an agglomerated microstructure composed fine grains with large voids. The average grain size was about 3-4 μm. The porosity decreased and the average grain size increased with increasing the sintering temperature and the PZT thick films sintered at 1050 °C showed the dense microstructure. On the other hand, the PZT thick films sintered at 1100 °C showed a large porosity due to the evaporation of PbO. The thickness of the PZT heterolayered thick films was about 60 μm.

Figure 4 shows the relative dielectric constant and the dielectric loss of PZT heterolayered thick films with variation of sintering temperature and frequency. The relative dielectric constant increased and the dielectric loss decreased with increasing the sintering temperature. These properties can be understood in terms of the effects of the grain growth, densification and the decreasing porosity, as shown in Fig. 3. The relative dielectric constant and dielectric loss of the PZT thick films sintered at 1050 °C were 445 and 1.90 % at 1 kHz, respectively. But, in the PZT thick films sintered at 1100 °C, the relative dielectric constant decreased and dielectric loss increased with increasing the porosity due to the PbO evaporation. PZT heterolayered thick films exhibit the superior dielectric (K=337) thick films[8]. We consider that there are constant compared with the single composition PZT(20/80) coexistence of tetragonal phase and rhombohedral phase or presence of the modified PZT phase at the interfaces between PZT(20/80) and PZT(80/20) films such as morpho-trophic phase boundary region in bulk PZT system[10].
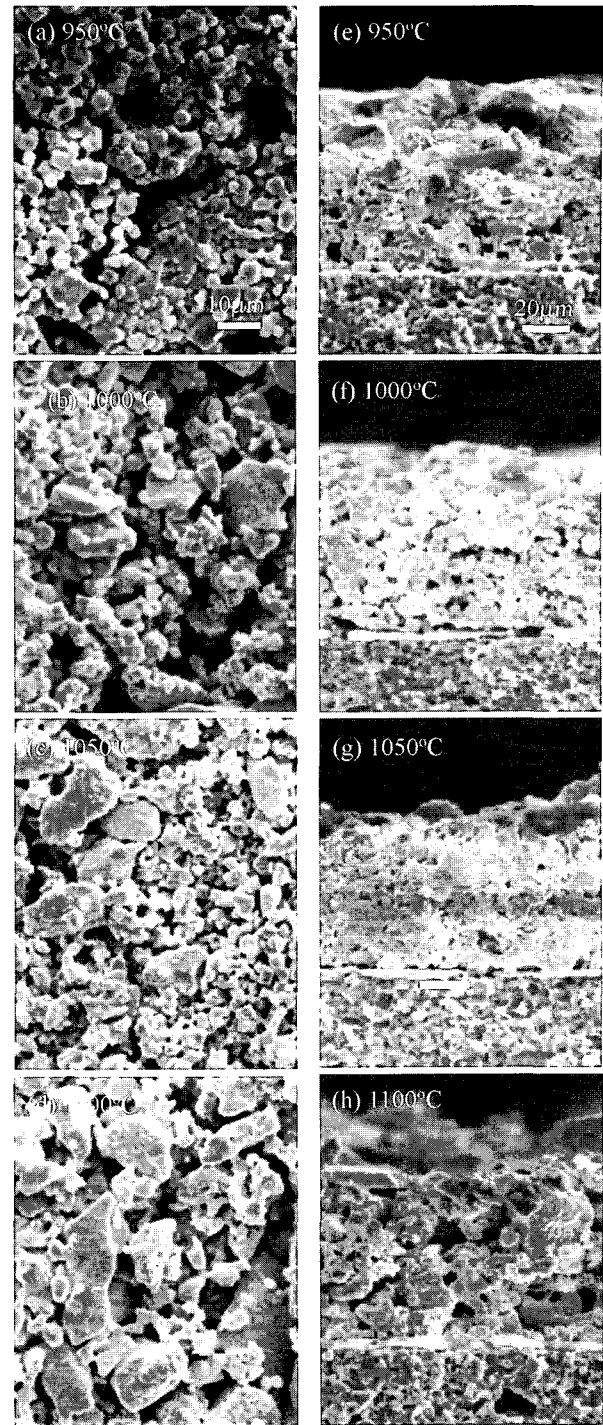

Fig. 3. Surface and cross-sectional SEM micrographs of the PZT heterolayered thick films for various sintering temperature.

And the dielectric constant decreased with an increase in the applied frequency. All specimens were showed the typical dielectric relaxation property[11].
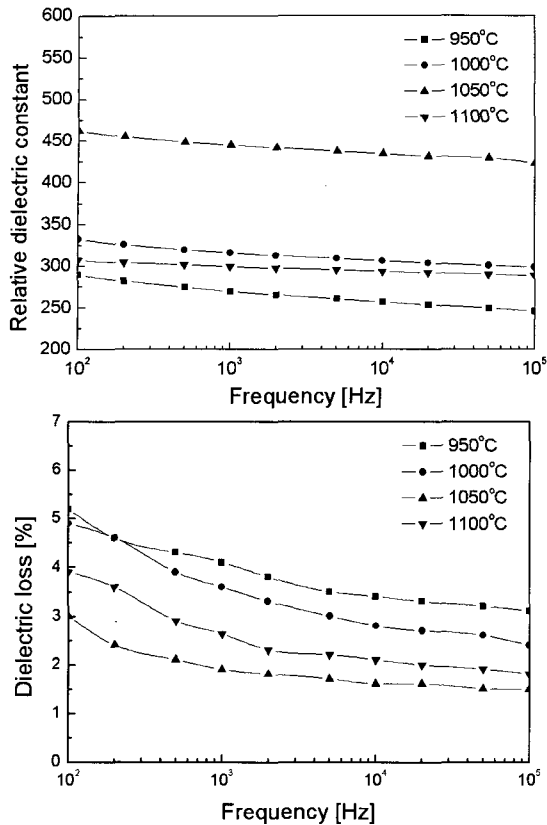
Fig. 4. Relative dielectric constant and dielectric loss of PZT thick films as function of sintering temperature and frequency.
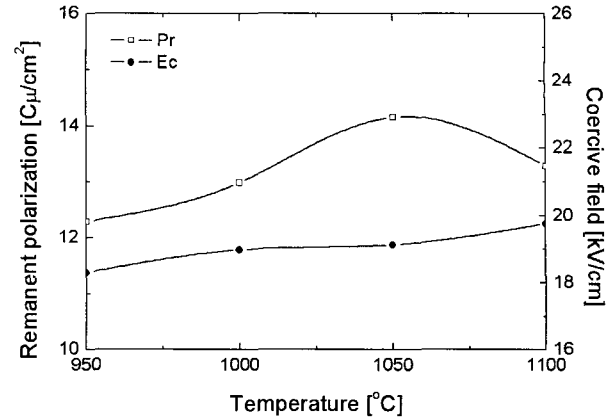

Fig. 5. Remanent polarization and coercive field of PZT thick films as a function of sintering temperature.

using PZT(20/80) and PZT(80/20) pastes. The optimal sintering conditions are temperature of 1050 °C and time of 2 h. The PZT heterolayered thick films sintered at 1050 °C showed the dense microstructure and thickness of about 60 μm. In the PZT heterolayered thick films fabricated by the screen-printing method, the effect of the lower PZT layers was not observed, because the thickness of the each layer is high. The relative dielectric constant and dielectric loss of the PZT thick films sintered at 1050 °C were 445 and 1.9 %, respectively. All specimens were showed the typical dielectric relaxation property. The remanent polarization and coercive field of the PZT thick films sintered at 1050 °C were 14.15 μC/cm^2, 19.13 kV/cm, respectively.

ACKNOWLEDGMENTS

Figure 5 shows the remanent polarization and coercive field of PZT heterolayered thick films with variation of sintering temperature. The remanent polarization and coercive field increased with an increase in a sintering temperature. These properties can be understood in terms of the effects of densification and growth of the ferroelectric grains. The porosity which created the depolarizing field decreased and the contact area of grains increased with an increase the sintering temperature[12]. In the PZT thick films sintered at 1100 °C, the remanent polarization decreased due to the PbO evaporation. The remanent polarization and coercive field of the PZT thick films sintered at 1050 °C were 14.15 μC/cm^2, 19.13 kV/cm, respectively.

4. CONCLUSION

In this research, PZT(20/80) and PZT(80/20) powders, prepared by using a sol-gel method, were mixed with an organic vehicle, and PZT heterolayered thick films were fabricated by screen-printing techniques by alternately

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