Structural and Electrical Properties of $Pb(Zr_{0.4}Ti_{0.6})O_3/Pb(Zr_{0.6}Ti_{0.4})O_3$ Heterolayered Thick Films

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Ferroelectric PZT heterolayered thick films were fabricated by the alkoxide-based sol-gel method. $Pb(Zr_{0.4}Ti_{0.6})O_3$ and $Pb(Zr_{0.6}Ti_{0.4})O_3$ paste were made and alternately screen-printed on the Al_2O_3 substrates. We have introduced a press-treatment to obtain a good densification of screen printed films. The porosity of the thick films was decreased with increasing the applied pressure and the thick films pressed at 60 MPa showed the dense microstructure and thickness of about 76 μm. The remanent polarization and coercive field increased with increasing applied pressure and the values for the PZT thick films pressed at 60 MPa were 17.04 $\mu C/cm^2$ and 78.09 kV/cm, respectively.

Keywords : PZT ceramics, Ferroelectric, Thick films, Screen-printing, Structural properties, Remanent polarization, Coercive field

1. INTRODUCTION

Ferroelectric $Pb(Zr,Ti)O_3$ (PZT) material is one of the most important electric ceramics materials for use in sensors, actuators, and filters, because of their unique properties. PZT has Tetragonal phase with rhombohedral phase according to the composition. PZT(52/48) has both tetragonl phase and rhombohedral phase. And the direction of polarization increases to 14 and has superior electrical characteristic. The phase did the coating different two composition and made heterolayered structure. Interest in applying PZT films to microactuators has been increasing recently. In most cases, films thicker than 10 m are required to obtain a large force effectively, though the optimum thickness depends on the structure and substrate material of the actuator. Generally, PZT thick films are fabricated on substrates, such as Al_2O_3 and ZrO_2, using a screen-printing method, and sintering temperatures above 1000 °C are required to fabricated dense thick films[1,2]. 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. Although it would be highly desirable to screen-print other components, such as capacitors, varistors, sensors, etc., currently this cannot be done while keeping the electrical properties of the corresponding ceramics. One of the main problems, inherent to this technology, is the lack of compactness of the screen printed layers[3].

In this study, PZT heterolayered thick films were prepared by the screen printing techniques, in which they were alternately screen-printed on high purity alumina substrates using $Pb(Zr_{0.4}Ti_{0.6})O_3$ and $Pb(Zr_{0.6}Ti_{0.4})O_3$ pastes. We have introduced a press-treatment of the green film printed on the substrates to obtain a good densification of screen printed films without inorganic binder. And the structural and dielectric properties of the thick films were investigated for fabricating various transducers and electronic devices.

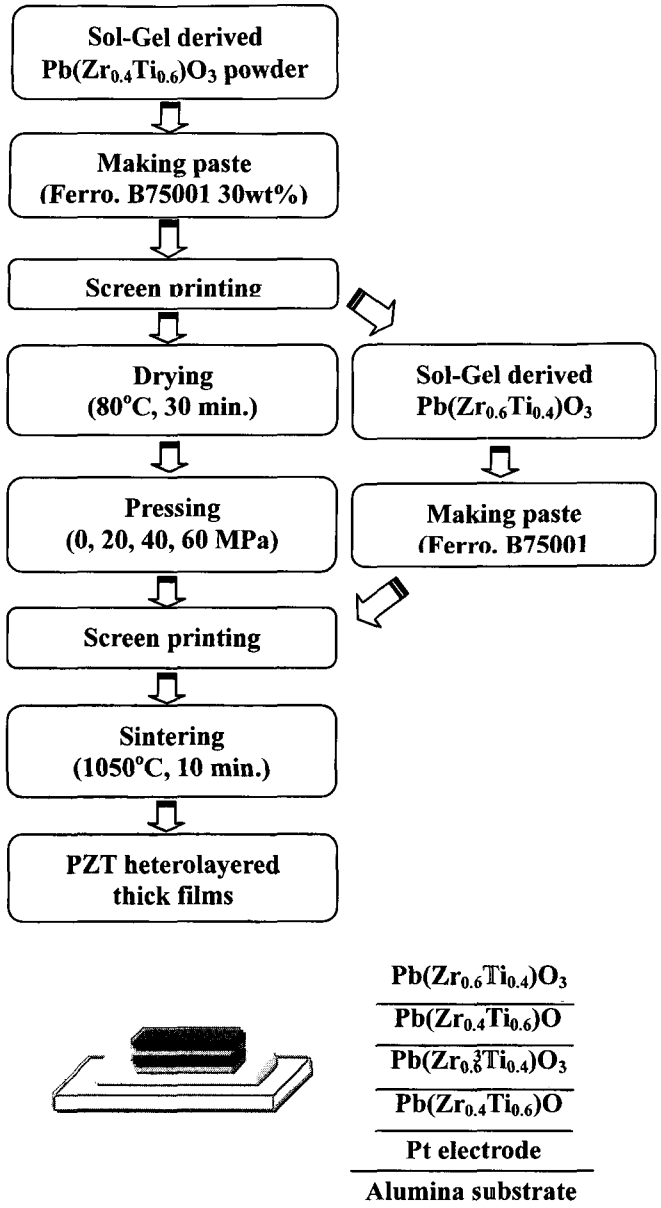

Fig. 1. Flowchart for the preparation and heating schedule of PZT heterolayered thick films.

2. EXPERIMENTAL PROCEDURE

$Pb(Zr_{0.4}Ti_{0.6})O_3$ and $Pb(Zr_{0.6}Ti_{0.4})O_3$ 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[4]. A 10 mol% excess of PbO was added to compensate for the lead loss during heat treatment.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 ($15\times15\times1$ mm^3). The $Pb(Zr_{0.4}Ti_{0.6})O_3$ paste was screen-printed on the substrates to form the first layer. These $Pb(Zr_{0.4}Ti_{0.6})O_3$ films were dried, and then the $Pb(Zr_{0.6}Ti_{0.4})O_3$ paste was screen-printed and dried on the $Pb(Zr_{0.4}Ti_{0.6})O_3$ films to form the second layer under the same conditions. This procedure was repeated 4 times. After removal of the solvents, the screen printed films were pressed at 0, 20, 40, 60 MPa using a hydraulic press. These heterolayered PZT thick films were sintered at 1050 °C for 10 min in PbO atmosphere. The crystalline structures of the PZT heterolayered thick films were analyzed by X-ray diffraction (XRD) with CuKα emission. The surface and cross-sectional microstructures of films were examined using scanning electron microscopy (SEM). 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) at 1 KHz. Ferroelectric properties were measured using a ferroelectric tester (Radiant, RT-66A).

3. RESULTS AND DISCUSSION

Figure 2 shows the X-ray diffraction patterns of the PZT heterolayered thick films printed on Pt/alumina substrate. PZT thick films showed the typical XRD patterns of a perovskite polycrystalline structure without preferred orientation and no pyrochlore phase is observed. And X-ray diffraction patterns of PZT thick films showed the coexistenced of the rhombohedral phase and tetragonal phase. But intensity of tetragonal

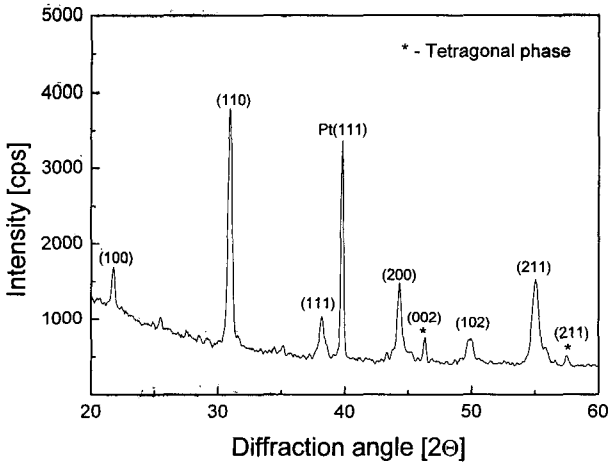

Fig. 2. X-ray diffraction patterns of the PZT heterolayered thick film.

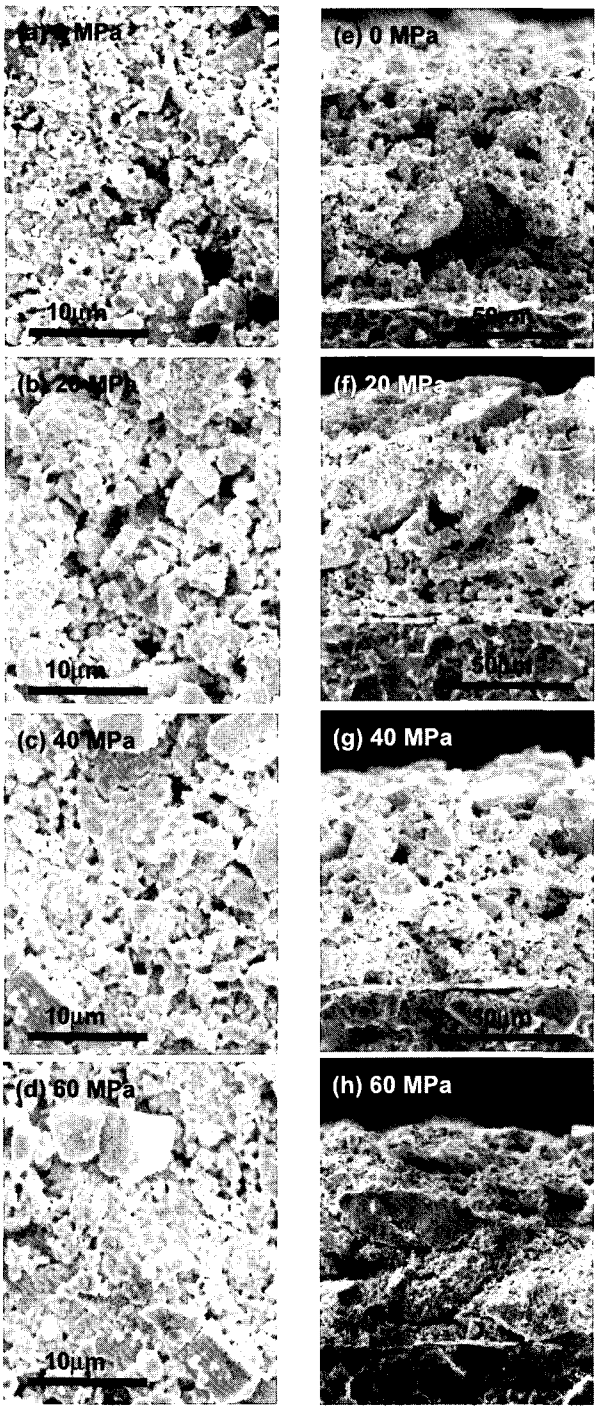

Fig. 3. SEM micrographs of surface and cross-section morphologies in PZT heterolayered thick films with variation of applied pressure.

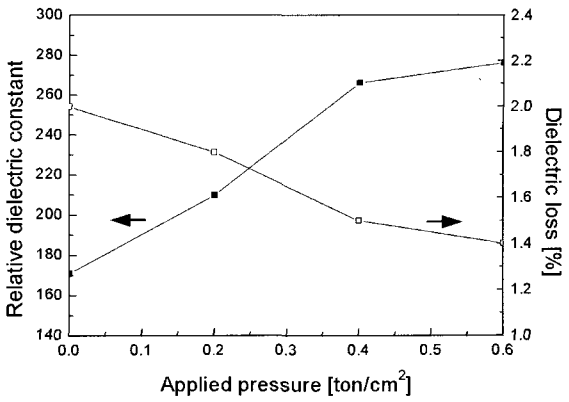

Fig. 4. Relative dielectric constant and dielectric loss of PZT heterolayered thick films as a function of applied pressure.

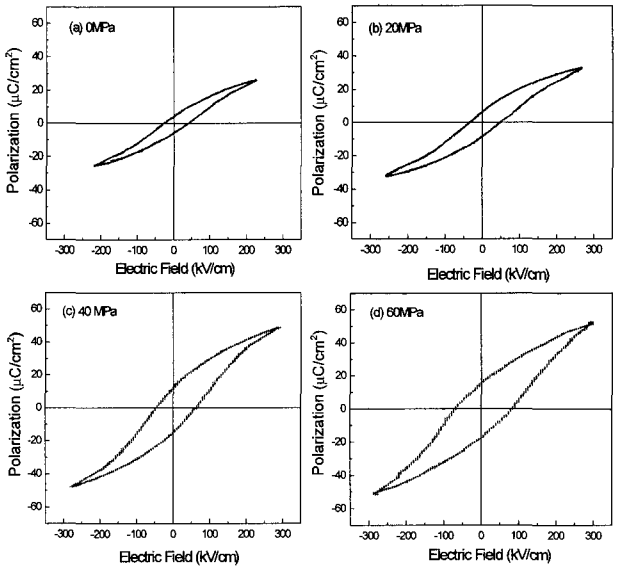

Fig. 5. P-E hysteresis loops of PZT thick films with variation of applied pressure.

phase showed compared with rombohedral phase so that it was low. This is because the thickness of PZT(60/40) thick films thick as the 15μm.

Figure 3 shows the surface and cross-section SEM micrographs of the PZT thick films printed on Pt/alumina substrate for various applied pressure. The average grain size was about 1-2 m. The rugosity and the porosity of the thick films were decreased with increasing the applied pressure and the thick films pressed at 60 MPa showed the dense microstructure and thickness of about 76 μm.

Figure 4 shows the relative dielectric constant and the dielectric loss of PZT thick films with variation of applied pressure. The relative dielectric constant increased and the dielectric loss decreased with increasing applied pressure. These properties can be understood in terms of the effect of the densification and the decreasing porosity, as shown in Fig. 2. The relative dielectric constant and dielectric loss of the PZT thick

films pressed at 60 MPa were 276 and 1.40 %, respectively.

Figure 5 shows the P-E hysteresis loops of PZT thick films with variation of applied pressure. The remanent polarization and coercive field increased with increasing applied pressure and the values for the PZT thick films pressed at 60 MPa were 17.04 $\mu C/cm^2$, 78.09 kV/cm, respectively. Thus, the better the densification of the films, the higher is the ferroelectric properties.

4. CONCLUSION

In this research, $Pb(Zr_{0.4}Ti_{0.6})O_3$ and $Pb(Zr_{0.6}Ti_{0.4})O_3$ 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 using $Pb(Zr_{0.4}Ti_{0.6})O_3$ and $Pb(Zr_{0.6}Ti_{0.4})O_3$ pastes. The effect of mechanical pressure on the electrical properties of PZT heterolayered thick films has been demonstrated. PZT thick films showed the typical XRD patterns of a perovskite polycrystalline structure without preferred orientation and no pyrochlore phase is observed. The densification of the thick films was increased with increasing the applied pressure. The relative dielectric constant and dielectric loss of the PZT thick films pressed at 60 MPa were 276 and 1.40 %, respectively.

ACKNOWLEDGMENTS

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