Preparation of Low-Temperature Fired PZT Thick Films on Si by Screen Printing

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(Received 4 February 2003, Accepted 27 February 2003)

Piezoelectric powder with the composition of $PbTiO_3$-$PbZrO_3$-$Pb(Mn_{1/3}Nb_{2/3})O_3$ and small particle size of 0.3 μm was investigated for low-temperature firing of PZT thick films. $PbTiO_3$-$PbZrO_3$-$Pb(Mn_{1/3}Nb_{2/3})O_3$ ceramics showed dense microstructure and superior piezoelectric properties, electromechanical coupling factor (k_p) of 0.501 and piezoelectric constant (d_{33}) of 224. The PZT paste was made of the powder and organic vehicles, and screen-printed on Pt(450nm)/YSZ(110nm)/SiO_2(300nm)/Si substrates and fired at 800~900℃. Any interface reaction between the PZT thick film and the bottom electrode was not observed in the PZT thick films. The PZT thick film fired at 800℃ showed moderate electrical properties, the remanent polarization(P_r) of 16.0 μC/cm², the coercive field(E_c) of 36.7 kV/cm, and dielectric constant (ε_r) of 531. Low-temperature sinterable piezoelectric composition and high activity of fine particles reduced the sintering temperature of the thick film. This PZT thick film could be utilized for piezoelectric microactuators or microsensors that require Si micromachining technology.

Keywords : Sintering, Piezoelectric properties, PZT, Thick films.

INTRODUCTION

Pb(Zr,Ti)O_3(PZT) piezoelectric ceramics have been applied to ultrasonic vibrators, filters, sensors, actuators and so on. Recently, microactuators and microsensors have been fabricated by micromachining piezoelectric thin and thick films.[1-4] PZT thick films thicker than 10 μm are required for microactuators or microsensors which need large strains or forces[4]. Screen printing method has been widely applied to thick film fabrications due to the cost effectiveness and simple manufacturing process[5,6]. PZT films should, however, be fired at low temperature for compatibility with silicon micromachining technology.

In most reports, screen printed PZT thick films have been fired at higher temperatures than 900℃ and ceramic substrates such as Al_2O_3 and ZrO_2 were used[5,7-10]. Many researchers could decrease the firing temperature of PZT thick films by using PZT powders with a large amount (more than 5 wt%) of glass frit or other low-temperature melting compound like PbO and/or PbF_2[1,5-11]. However, reaction compounds, which deteriorate dielectric and piezoelectric properties, are formed at the interface between the PZT thick film and the Si substrate when PZT thick films with a large amount of glass frit were fired at high temperatures.[5,8] Jones et al. reported that PZT thick films could be fired at low temperature under extended firing time[11]. They fabricated PZT thick films by firing at 800℃~850℃ for 6 hours. However, they observed a reaction at the interface because they made PZT paste of PZT-5H powders with a large amount of glass frit, 5 wt% lead borosilicate. Y. Akiyama et al. fired $Pb(Ni_{1/3}Nb_{2/3})O_3$-$PbZrO_3$-$PbTiO_3$ thick films with only 1 wt% glass frit at 900℃[10]. However, the thick film showed poor electrical property, remanent polarization of 5.7 μ C/cm². And the firing temperature of PZT thick films on Si should be lower than 850℃ to prevent the formation of non-piezoactive reaction compounds at the interface[11].

In this study, a low-temperature sinterable ternary solid solution system of $PbTiO_3$-$PbZrO_3$-$Pb(Mn_{1/3}Nb_{2/3})O_3$ with no glass frit except 1 wt% excess PbO was used and the powder was pulverized into an average particle size of 0.3 ㎛ for reducing firing temperature of the thick film. The densification, microstructure and the piezoelectric properties of the ceramics were examined. The PZT paste was made of the powder and organic vehicles, and screen-printed on Pt(450nm)/YSZ(110nm)/SiO_2(300nm)/Si substrates and fired at 800℃ ~900℃. The microstructure and electrical properties of the PZT thick films were investigated.

2. EXPERIMENTAL PROCCEDURE

$PbTiO_3$-$PbZrO_3$-$Pb(Mn_{1/3}Nb_{2/3})O_3$ with 1wt% PbO was used as a piezoelectric powder in this work. Some additives less than 0.5 mole% were added in the powder to enhance piezoelectric properties. The powder was pulverized into an average particle of 0.3 ㎛ by attrition milling. Ceramic samples were prepared by conventional process. They were sintered at 800~900℃ for 2 hours. Silver paste were printed on the surfaces of the samples and annealed at 600℃ for 30 min. The ceramic samples were poled under 2.5 kV/cm for 30 min. at 100℃.

For the preparation of the thick film paste, the powder was mixed with organic vehicle consisting of ethyl-cellulose and α -terpineol in a three roll mixer and a conditioning mill. Yttrium stabilized zirconia(YSZ) was deposited at 600℃ on the SiO_2(300nm)/Si substrate as a diffusion barrier by RF magnetron sputtering. As-deposited YSZ thin films were annealed 900℃ for 30 min. in O_2 for further crystallization. Pt bottom electrode was deposited on YSZ/SiO_2/Si at 400℃ by DC magnetron sputtering. PZT paste was screen-printed on the Pt(450nm)/YSZ(110nm)/SiO_2(300nm)/Si substrate, leveled at room temperature for 10 minutes, and dried at 150℃ for 15 minutes. This process was repeated three times. PZT thick films were fired at 800~900℃ for 2 hour after organics were burned out at 500℃ for 1 hour. Firing was performed in PbO atmosphere. Mixed powders of $PbZrO_3$ and 10 mol% ZrO_2 were used to control the PbO atmosphere. The thickness of the fired PZT thick film was 20~30 ㎛. Pt top-electrodes were deposited on the fired PZT thick film at room temperature using a shadow mask with holes of 260 ㎛ by DC magnetron sputtering and annealed at 600℃ for 10 minutes in air to improve interface properties.

Phases were identified using an X-ray diffractometer (Shimadzu, XD-D1) and microstructures were observed using a field emission scanning electron microscopy (Hitachi, S-4300). Capacitances and dielectric losses were measured using an impedance analyzer (HP4192A). Ferroelectric P-E hysteresis loops were measured using a ferroelectric tester (Radiant Technologies, Inc., RT66A) and a high voltage amplifier (Radiant Technologies, Inc., RT66A HVI).

3. RESULTS AND DISCUSSION

Perovskite single phases with tetragonal structure were confirmed in the X-ray diffraction patterns of the all sintered ceramic samples. Figure 1 shows the surface microstructures of the ceramics sintered at (a) 800, (b) 850, and (c) 900℃. All samples show dense microstructures and average grain size increased from 1.2 to 2.22 ㎛ with increasing the sintering temperature from 800 to 900℃.

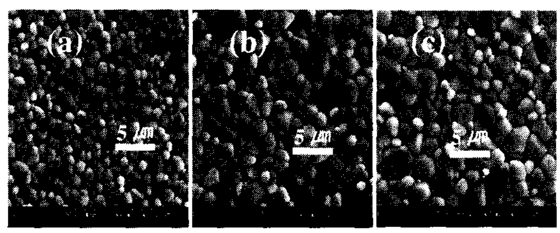

Fig. 1. The microstructures of the PZT ceramics sintered at (a) 800, (b) 850 and (c) 900℃.

Table 1. Electrical properties of the PZT ceramics sintered at (a) 800, (b) 850 and (c) 900℃.

Sintering Temp.	Linear Shrinkage (%)	ε_r	tanδ (%)	kp (%)	d_{33} (pC/N)	Pr (μC/㎠)	Ec (kV/cm)
800℃	14.89	1168	0.45	50.1	224	16.2	19.1
850℃	15.06	1196	0.43	50.2	254	17.2	19.5
900℃	15.31	1225	0.42	50.4	263	16.2	19.1

Physical and electrical properties of the sintered ceramics are shown in Table 1. Linear shrinkage increased and electrical properties were enhanced when the sintering temperature increased. As shown in Table 1, the PZT ceramics sintered at 800~900℃ had superior piezoelectric properties. Piezoelectric properties of the PZT ceramic sintered at 800℃ are as follows; electromechanical coupling factor (k_p) of 50.1%, piezoelectric constant(d_{33}) of 224 and dielectric constant (ε_r) of 1168 at 1 kHz.

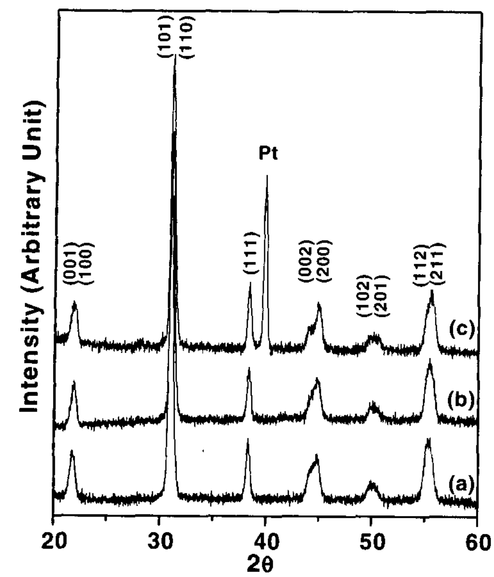

Fig. 2. X-ray diffraction patterns of PZT thick films fired at (a) 800, (b) 850 and (c) 900℃.

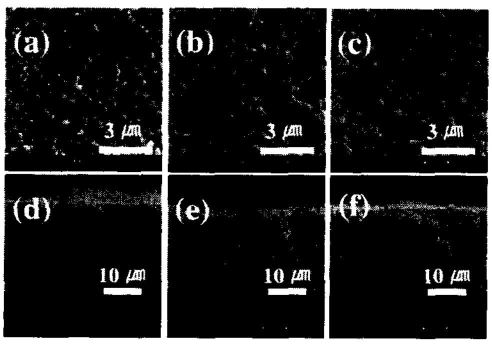

Fig. 3. Surface and cross-section morphologies of PZT thick films fired at (a), (d) 800 (b) , (e) 850, and (c), (f) 900℃.

Figure 2 shows X-ray diffraction patterns of PZT thick films fired at (a) 800, (b) 850, and (c) 900℃. No second phase is shown in X-ray diffraction patterns of the PZT thick films. Figure 3 shows the surface and cross-sectional morphologies of the PZT thick films fired at (a), (d) 800, (b), (e) 850, and (c), (f) 900℃. The thick films have smaller grain sizes and porous microstructures as compared to the microstructures of the ceramic samples in Fig. 1. Average grain size and the density increased with increasing the firing temperature as shown in Fig. 3. Thick films fired at 800~900℃ show clear interfaces between PZT thick films and Pt bottom electrodes in Fig. 3 (d)~(f). It is ascribed to the piezoelectric composition with small amounts of low-temperature melting phase in this work. And YSZ buffer layer seem to be also very effective in protecting inter-diffusion and chemical reaction at the interface.

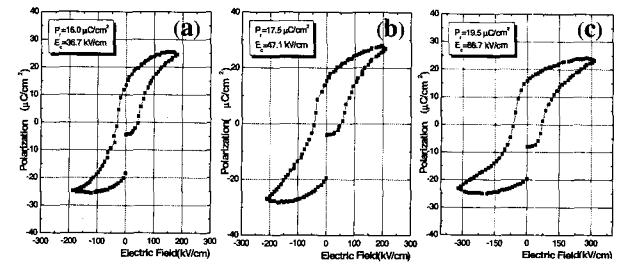

Fig. 4. P-E hysteresis loops of PZT thick films fired at (a) 800, (b) 850 and (c) 900℃.

Ferroelectric P-E hysteresis loops of the PZT thick films sintered at (a) 800, (b) 850, and (c) 900℃ are shown in Fig. 4. PZT thick films show typical ferroelectric P-E hysteresis loops. The remanent polarization (P_r) of the PZT thick film increased and the P-E hysteresis loop became more square-shaped with increasing the firing temperature. Larger grain size and denser microstructure of the PZT thick film fired at higher temperature seem to induce higher remanent polarization. The dielectric constant of the PZT thick film fired at 800℃ was 531 at 100 kHz. The remanent polarization and the coercive field of the PZT thick film fired at 800℃ were 16.0 μ C/㎠ and 36.7 kV/㎝, respectively. These ferroelectric properties are comparable to those of PZT ceramics. PZT powders with low-temperature sinterable ternary piezoelectric composition and small particle size reduced effectively the firing temperature of the thick film. Since the PZT thick film is sinterable at low temperature, 800℃, enough to be compatible with Si micromachining technology and shows well-developed P-E hysteresis loop, these films could be utilized for piezoelectric microactuators or microsensors.

4. CONCLUSION

With piezoelectric powders with the ternary composition of $PbTiO_3$-$PbZrO_3$-$Pb(Mn_{1/3}Nb_{2/3})O_3$ doped by 1wt% PbO and small particle size of 0.3 ㎛, PZT thick films were fabricated on $Pt/YSZ/SiO_2/Si$ substrates by screen printing method. Densification and electrical properties of the thick film improved with increasing the firing temperature. Any reaction compound was not observed at interface between the PZT thick film and the bottom electrode in the PZT thick films fired at 800~900℃. The PZT thick film fired at 800℃ showed moderate electrical properties, the remanent polarization of 16.0 μ C/㎠, the coercive field of 36.7 kV/cm, and dielectric constant (ε_r) of 531. The PZT powder with low-temperature sinterable ternary composition and small particle size was effective in reducing the firing temperature of the PZT thick film.

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