Lead zirconate titanate (PZT) thick films with uniformly dispersed submicrometer pores were successfully fabricated on platinized silicon substrates with various thicknesses ranging from 1 μm to over 100 μm by aerosol deposition. Mixed powders of PZT and polyvinylidene fluoride (PVDF) were deposited for initial fabrication of composite films. After burn-out of the PVDF phase from the composite films during postannealing processing at 700 °C, uniformly dispersed submicrometer pores capable of relaxing the residual stress were generated in the PZT thick films. The dielectric and piezoelectric properties were improved with increasing film thickness due to the minimization of the interfacial clamping effect.

I. Introduction

Piezoelectric ceramic films have a wide range of applications such as sensors, actuators, micro-ultrasonic motors, micro-electro-mechanical systems, energy harvesting, and ultrasonic devices. The film thickness required for high sensitivity, transduction, or actuation ranges from 1 to 100 μm. Especially for physical sensor applications, such as tactile/pressure sensors and structure healthy monitor sensors, the output signal can be dramatically increased by increasing the film thickness, which necessitates thick films with a thickness ranging from 1 to 100 μm. However, thin films or bulk materials cannot fulfill this thickness range.

With traditional deposition processes, such as sol–gel, sputtering and chemical vapor deposition, it is difficult to make films thicker than 10 μm due to their low deposition rate (about 1 μm/h) and high interfacial stress. Screen-printing is a well-known process capable of generating thick films with a very high production rate. However, these processes suffer some shortcomings such as applicable substrate materials, low sintered density, high sintering temperature (typically over 900°C), weak adhesion strength between the film and substrate, and quite porous microstructure with large pores. A process capable of forming films with a thickness in the range of 1 to 100 μm is urgently required to satisfy the needs of various applications.

The aerosol deposition (AD) technique can be used to fabricate thick films at room temperature (RT) by consolidation of submicrometer-sized ceramic particles with substrates. Many previous studies, including Akedo and colleagues and our own, have already presented details on AD. The ceramic films made by AD have much higher internal stress and small crystallite size (generally several to tens of nanometers), resulting in poor piezoelectric properties. Postannealing the films to induce grain growth can improve their electrical properties. Nevertheless, internal stress will cause delamination during postannealing. Miyoshi removed the substrate to exclude the influence of the substrate-induced stress effect. After annealing at 1100°C for 3 h, the value of the free-standing films was 410 pC/N, which is comparable to that of bulk PZT ceramics. However, substrate removal is not practical in real applications.

II. Experimental Procedure

Commercially available, PZT-based, piezoelectric ceramic powder (Pb(Al1/3Nb2/3)O3–Pb(Zr,Ti)O3, KP10, Kyungwon Ferrite Ind. Co., Shihueung, Korea) and PVDF polymer powder (99.9% purity, Aldrich Co., Milwaukee, WI) were used as the raw powders. As such commercial PZT powder is not fully crystallized and contains a small amount of excess PbO, the powder was calcined at 900°C for 2 h, and then crushed by planetary milling for 6 h to obtain an appropriate particle size. The ceramic powder was then mixed with 3 vol% of PVDF powder by ball milling with high-purity 3Y-TZP (tetragonal zirconia polycrystalline) ball media and ethanol in a high density polyethylene jar for 1 h. The mixed slurry was then dried at ~70°C to form a ceramic–polymer composite powder. The average particle size (d50) of the composite powder was ~1.3 μm. A nozzle with a rectangularly shaped orifice of 5 mm × 0.4 mm and a gas flow of 3 L/min were used for the film deposition on the platinized silicon wafer. By controlling the scan cycle times, PZT–PVDF composite films with a thickness range of 1–130 μm were formed on the silicon wafer substrates. All the films were annealed at 700°C for 1 h to generate pores as a stress relaxor and induce grain growth of the PZT crystallites.

The phases of the starting powders and the deposited films were identified by X-ray diffraction (XRD: D-MAX 2200, Rigaku Co., Tokyo, Japan). The film microstructures were observed using scanning electron microscopy (SEM: JSM-5800, JEOL Co., Tokyo, Japan). A Pt top electrode with a diameter of either 1 or 3 mm was deposited on the film by DC sputtering in order to measure the electric properties. The dielectric properties were measured by using an impedance analyzer (4294A, Agilent Technologies, Santa Clara, CA). The polarization–field hysteresis loops were measured at 100 Hz by a standardized
III. Results and Discussion

The XRD patterns of the crystal phases of the starting PZT–PVDF composite powder and the films prepared on the platinumized silicon wafer substrate are shown in Fig. 1. All the films were annealed at 700°C for 1 h. The powder and all the variously thick films exhibited a perovskite structure without any secondary phases, including pyrochlore or PbO. PVDF addition did not affect the crystal structure or phase stability of the PZT thick films. The film intensities were as high as that of the powder, indicating that grain growth had occurred during annealing.

Figure 2 shows the fractured cross-sectional SEM micrographs of the films with different thicknesses after postannealing at 700°C for 1 h. The film thicknesses, which were controlled by the nozzle scanning cycles, were around 1, 20, 100, and 180 μm, as measured in the micrographs. Although PZT films >180 μm thick were fabricated, they were not uniformly deposited and thereby showed severe thickness deviations. Therefore, we analyzed the properties of the films up to a thickness of 130 μm. The annealed films maintained good adhesion with the platinumized silicon wafer substrates, without any delamination, even at a film thickness exceeding 100 μm. As aforementioned, Choi et al.13 have fabricated ~20-μm-thick PZT–PVDF films with good properties; however, the film thickness was limited to 20 μm, possibly due to improper particle size. During the AD process, the particles were accelerated by the high pressure difference between the aerosol and deposition chambers. The particles accelerated to very high speed collided with the substrate to form ceramic coatings. Three phenomena occurred during collision: ceramic film formation, etching of the previously deposited film or substrate, and powder compaction. A particle size inadequate for AD leads to etching or compacting, thereby preventing any deposition. Therefore, the particle size of the ceramic powder for AD is assumed to be one of the most important factors for the fabrication of thick films. Hence, the particle size of the PZT and PVDF mixture powder was precisely controlled by planetary and ball milling, as described above in the experimental section.

Compared with the PZT films fabricated by other processes such as sol–gel and sputtering, very thick films can be deposited by AD in a relatively short time, as aforementioned. In general, films of thickness <1 μm can be deposited by one cycle of the sol–gel and sputtering process. The fabrication of thick films with a thickness over 10 μm by this conventional thin film process requires multiple deposition and thermal annealing, which is very time consuming.

Figure 3 presents a different magnification cross-sectional SEM microstructure of the 100-μm-thick film after 700°C annealing. The film showed good adhesion with the silicon substrate after annealing (Fig. 3(a)). The microstructure of the film is uniform from the bottom to the top (Fig. 3(b)). As shown in the higher magnification micrograph of Fig. 3(c), platelet-like pores were uniformly dispersed along parallel to the substrate surface, which were formed by PVDF burn-out. During deposition at RT, the secondary particles (in this study, PVDF) are dispersed in the matrix phase with a submicrometer-sized, platelet-like shape perpendicular to the particle spraying direction (i.e., parallel to the substrate surface direction),22,23 which can act as a stress relaxor. During annealing at 700°C, the PVDF phase burns out and the remaining pores can also relax the stress induced during the postannealing cooling down period. Although thick films can also be fabricated by screen printing, numerous organic vehicles and sintering additives are usually required and, moreover, high temperature sintering at over 900°C is imperative. The resulting porous sintered film with large pores (normally several micrometer) has poor properties.24,25 Furthermore, the need to prevent any reaction between the substrates and the films necessitates the formation of diffusion layers.26

Figure 4 presents the relationship of the dielectric constant and the dielectric loss according to the driving frequency for different films thicknesses. The dielectric constants of all films gradually decreased with increasing frequency, and were significantly improved with increasing thickness. The dielectric losses were <4% for all films. The dielectric constant and loss at 1 kHz are plotted according to thickness in Fig. 5. The dielectric losses were low for all the film thicknesses in the range of 1–130 μm, as aforementioned. The dielectric constant increased with increasing thickness up to 80 μm thick, and then plateaued.

Figure 6 shows the 100 Hz P–E hysteresis loops of the annealed films of different thicknesses at RT. Figure 6(a) gives the P–E loops at the electric field of 100 kV/cm. The saturated and remnant polarization increased with increasing film thickness up to 80 μm, after which the curves did not change markedly. Combining with Fig. 7, which shows the variation of $P_r/P_s$ at 100 kV/cm according to thickness, the $P_r/P_s$ also became saturated after 80 μm, in agreement with the tendency of the dielectric properties. Figure 6(b) shows the P–E loop at the maximum driving fields for each thickness. From 1 to 55 μm, an electric field of up to 500 kV/cm could be applied in all the films, with typical ferroelectric characteristics being exhibited.
However, at thicknesses exceeding 80 µm, the films were broken down at much lower fields of around 200 kV/cm. According to Gerson and Marshall\textsuperscript{27} and Chen \textit{et al.}\textsuperscript{28}, the dielectric breakdown strength decreases with sample thickness and then becomes saturated in general. The breakdown strength of PZT ceramics and thick films is dependent on the defect (generally pores) size and volume fraction in the ceramics/films. Although the microstructure was not strongly affected by the film thickness in this study, the breakdown strength may have been reduced because the number of pores in the films increases with increasing film thickness. This phenomenon affected the poling process and prevented the complete stabilization of piezoelectric properties due to the unstable polarization.

The much higher stress that is known to exist near the interface between the substrate and the film renders the domain motion difficult, in an effect termed the interface clamping effect. With increasing film thickness, the interface clamping effect is decreased until after a certain critical thickness, at which point the stress is reduced to zero and the interface clamping effect is minimized and saturated at the level of the bulk materials after the critical thickness.\textsuperscript{29} This explains the incremental increase in all the above properties with increasing thickness up to a saturation level at 80 µm.

The piezoelectric properties were affected by the film thickness, as shown in Fig. 8. Similar with the other properties, the effective piezoelectric constant $d_{33}^{\text{eff}}$ and the piezoelectric voltage constant $g_{33}^{\text{eff}}$ increased with increasing film thickness. However, contrary to our expectation, these piezoelectric properties did not become saturated as the thickness exceeded 80 µm. As aforementioned, the breakdown voltage of the thicker films was quite low. When an electric field slightly over 60 kV/cm was applied during poling at high temperature, radial cracks

![Image](image1)

**Fig. 3.** Fracture-sectional scanning electron micrographs of 700°C annealed, 100-µm-thick, AD-PZT film: (a) low magnification, (b) magnification of the red square in (a), and (c) high magnification micrograph from inside of the film.

![Image](image2)

**Fig. 4.** Dielectric constants and losses according to the frequency of 700°C annealed AD-PZT films on silicon substrate with different thicknesses.

![Image](image3)

**Fig. 5.** Dielectric constants and losses at the frequency of 1kHz according to film thickness for 700°C annealed AD-PZT films on silicon substrate.
were produced in the thicker films due to lateral clamping stress from inactive film.9 Under high electric field, the active film (electrode area) shrinks along the radial direction because of domain orientation, but the inactive film (unelectrode area) clamps this shrinkage. This lateral clamping stress is proportional to the piezoelectric constant. If the lateral clamping stress is higher than the mechanical strength of the film, radial cracks can be formed to relieve the stress. It is known that cracking can cause charge leakage and affect the piezoelectric properties of the film.28,30 Therefore all the thicker films were poled at very low fields that were insufficient for adequate poling of the samples. We can assume that the films thicker than 80 μm were partially poled, suggesting that the obtained $d_{33}^{\text{eff}}$ values do not reflect the real $d_{33}$ values of thicker films.

Table I presents a summary of the film properties at different thicknesses. The $d_{33}^{\text{eff}}$ and $g_{33}^{\text{eff}}$ values were maximized in the 55-μm-thick film at 210 ± 20 pm/V and 37.9 ± 3.6 V/m/N, respectively.

**IV. Conclusion**

The introduction of small and controlled pores capable of relaxing the internal stress of the film facilitated the AD fabrication of films ranging in thickness from 1 to 130 μm. All the films exhibited a uniform and dense microstructure, with no second phase after annealing at 700 °C. The dielectric losses were lower than 4%. The dielectric constant, saturated and remnant polarization of the films increased with increasing film thickness up to a saturated level, which was attributed mainly to the minimization and saturation of the interfacial clamping effect at thicknesses above 80 μm. The piezoelectric properties were also improved with increasing film thickness. The $d_{33}^{\text{eff}}$ and $g_{33}^{\text{eff}}$ values were maximized in the 55-μm-thick film at 210 ± 20 pm/V and 37.9 ± 3.6 V/m/N, respectively. The piezoelectric properties did not continue to increase as the thickness was increased above 80 μm, possibly due to insufficient poling because of the high lateral clamping effect and cracking.

**Table I. The Properties of 700 °C Annealed Aerosol Deposited (AD) PZT Films with Different Thicknesses**

<table>
<thead>
<tr>
<th>Thickness (μm)</th>
<th>As-deposited 20</th>
<th>1</th>
<th>15</th>
<th>30</th>
<th>55</th>
<th>80</th>
<th>130</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_r$ (at 1 kHz)</td>
<td>152</td>
<td>496</td>
<td>511</td>
<td>619</td>
<td>625</td>
<td>991</td>
<td>842</td>
</tr>
<tr>
<td>$\tan \delta$ (at 1 kHz)</td>
<td>0.0471</td>
<td>0.0285</td>
<td>0.032</td>
<td>0.0417</td>
<td>0.0379</td>
<td>0.0361</td>
<td>0.0369</td>
</tr>
<tr>
<td>$d_{33}^{\text{eff}}$ (pm/V)</td>
<td>—</td>
<td>75 ± 25</td>
<td>160 ± 40</td>
<td>150 ± 10</td>
<td>210 ± 20</td>
<td>115 ± 15</td>
<td>105 ± 5</td>
</tr>
<tr>
<td>$g_{33}^{\text{eff}}$ (10⁻³ V/m/N)</td>
<td>—</td>
<td>17.1 ± 5.7</td>
<td>35.4 ± 8.8</td>
<td>27.3 ± 1.8</td>
<td>37.9 ± 3.6</td>
<td>13.1 ± 1.7</td>
<td>14.1 ± 0.7</td>
</tr>
</tbody>
</table>

Fig. 6. $P–E$ hysteresis loops of 700 °C annealed AD-PZT films on silicon substrate with different thicknesses: (a) at 100 kV/cm and (b) at saturated electric fields.

Fig. 7. Remnant and saturated polarizations of 700 °C annealed AD-PZT films according to thickness in 100 kV/cm fields on silicon substrate.

Fig. 8. Variation in the effective piezoelectric coefficient $d_{33}^{\text{eff}}$ and piezoelectric voltage constant $g_{33}^{\text{eff}}$ according to films thickness of 700 °C annealed AD-PZT films on silicon substrate. Open symbols indicate insufficiently poled samples.
Effect of Film Thickness on the Piezoelectric Properties

References


