Fabrication of thick Pb(Zr,Ti)O₃ (PZT) films by modified sol–gel methods for application in MEMS

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Abstract—Pb(Zr,Ti)O₃ (PZT) films with thickness ranging from 2 µm to 10 µm have successfully been prepared using the sol–gel-based ceramic–ceramic 0-3 composite method, polyvinylpyrrolidone (PVP)-assisted sol–gel method and electrostatic spray deposition (ESD) with satisfied film properties on Pt/Ti/SiO₂/Si substrate. Using PVP and PZT powders as additives, the critical thickness of sol–gel derived PZT film can be sufficiently increased to 0.9 µm and 0.5 µm, respectively. The crystal-orientation of the films was investigated by X-ray diffractometer. It was found that the use of buffer layer was effective to affect the film’s nucleation and growth behavior and enhance the pervoskite (100) orientation. According to the atomic force microscope images, these films exhibit uniform grain size distribution. The relative dielectric constants of the film prepared by these modified sol–gel techniques, 1050, 600 and 960, were measured, which are satisfied for application in MEMS.

Keywords: PZT; sol–gel; PVP; powder; ESD; film; MEMS.

1. INTRODUCTION

Fabricating small devices that are almost invisible has been one of the dreams of many researchers. Miniaturization will lead to various attractive improvements in efficiency, functionality, performance and stability besides its cost-saving batch process, low power consumption and environmental competitiveness [1]. During recent years, the development of microelectromechanical system (MEMS), where mechanical structure, such as microsensors and microactuators, are well integrated with electronic circuits, has shown us significant opportunities for miniaturizing the device to micrometer even nanometer range. Remarkable progresses have been made in design, optimization and fabrication. Accelerometer [2], ink-jet head [3] and DLP [4] are representative examples of MEMS in practical use.

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As one of the most useful functional materials, Pb(Zr,Ti)O$_3$ (PZT) is of great interest in MEMS as an electromechanical conversion medium for its excellent mechanical and piezoelectric properties [5]. Based on PZT film, Kunz et al. successfully developed a novel triaxial silicon accelerometer with integrated detector, which has a much higher sensitivity than that of previously presented approaches and is significantly smaller [2]. PZT films are also being used in self-sensing and self-actuating microcantilever array for mass storage applications. The longitudinal resolution of each cantilever can be as high as 0.1 nm [6, 7]. PZT was believed to be one of the most promising sensing and actuating material for MEMS applications in near future [5].

For application in MEMS, especially for powerful microactuators such as micro-motors [8], microscanners [9], ultrasonic high-frequency transducers [10], etc., PZT films with great film thickness, from several to a hundred $\mu$m, as well as excellent film properties, including high dielectric constant and high piezoelectric constant, are preferred to achieve high sensitivity, great displacement and supply sufficient power. Recently, the tremendous growth of research on PZT film fabrication has resulted in the development of many sophisticated PZT film-synthesis techniques. Among these methods, sol–gel [11] is the most popular and widespread technique for PZT film fabrication in MEMS for its attractive advantages of simple setup and excellent film properties. In this method, PZT precursor solution was spin-coated on substrate then annealed at high temperature, high volume shrinkage due to solvent evaporation will make cracks during anneal, which results in low critical thickness of about 120 nm in each layer. Therefore, PZT films with thickness of more than 2 $\mu$m are difficult to obtain by this method. The hydrothermal method utilizes the chemical reaction between ions melted in the solution [12]. Great film thicknesses, of up to 10 $\mu$m, can be obtained, but this method is difficult to be compatible with the arts and crafts of MEMS for its high reaction temperature and high atmospheric pressure of about several atm [13]. Sputtering describes the physical transfer of atoms from a target to a substrate as a result of momentum transfer, a standard IC fabrication technique for film deposition. This technique can be used to produce thick PZT film of several $\mu$m with large area coverage, but it is difficult to control the composition of the film for the different sputtering rate between Pb, Zr and Ti [14]. Rotating target sputtering and multi-target sputtering were proposed at the cost of complex equipment and hard operation [15]. As a promising technique for the preparation of multi-component oxide films, pulsed laser ablation (PLA) has also been introduced into PZT film fabrication by Otsubo et al. [16] and proved to be pretty good in terms of the capability for producing stoichiometric films, but it has problems in large film coverage and cost-saving batch process because of its restricted laser spot size. Other methods, such as chemical vapor deposition (CVD) [17] and jet molding system [18], are difficult to meet the demands of MEMS on properties of the PZT film. Thus, developing new fabrication techniques for the preparation of PZT films with both satisfying film properties and great thickness of
more than 2 \( \mu m \) is imperative to promote the application of this attractive piezo-electric material in MEMS.

Although the main limitation in sol–gel processing is the film thickness that is achievable, this method is still believed as the most promising technique in MEMS for its simple set-up and excellent film properties. Many modified sol–gel processes have been proposed to increase the critical thickness of the film in recent years [19, 20]. So far, the use of additives, such as polyvinylpyrrolidone (PVP) and PZT powder, into sol–gel solution are reported to be significantly effective in increasing the critical thickness of sol–gel derived PZT films [21, 22]. In a previous study [23], electrostatic spray deposition (ESD) has also been proven to be a promising technique for the preparation of thick PZT film with acceptable film properties. In this paper, we report our progresses on these modified sol–gel methods for PZT film preparation, including sol–gel based ceramic–ceramic 0-3 composite method, PVP assisted sol–gel method and ESD, where the numbers 0 and 3 describe the connectivity of the PZT powder and the sol–gel matrix, respectively [22]. The orientation of the PZT film is believed to be the most important factor affecting the PZT film’s piezoelectric properties. Therefore, the orientation of the as-deposited PZT films was investigated. Furthermore, the microstructures and electric properties of the films were observed and measured. The basic phenomena occurring during the preparation was analyzed. The advantages and problems of each method were also compared and discussed.

2. EXPERIMENTAL

In our experiments, the PZT precursor solution was prepared by the sol–gel method using zirconium n-propoxide \((\text{Zr}(\text{C}_3\text{H}_7\text{O})_4)\), titanium tetraisopropoxide \((\text{Ti}((\text{CH}_3)_2\text{CHO})_4)\) and lead acetate \((\text{Pb}(\text{CH}_3\text{COO})_2)\) as original materials, as described in detail elsewhere [24]. Strongly (111) orientated platinum film with thickness of 150 nm was deposited on SiO \(_2\)/Si substrate as bottom electrode by sputtering. Titanium layer of 50 nm in thickness was used as intermediate layer to enhance the adherence between the platinum and the substrate.

Many techniques, such as ultrasonic spray pyrolysis [25] and sol–gel [26], can be applied for PZT powder preparation. In our experiment, PZT powder was prepared by sol–gel combustion as follows: First, the PZT solution was put into a crucible, then it was heated to 120°C for solvent evaporation, 450°C for pyrolysis of organic residues and finally annealed at 600°C for pervoskite phase crystallization. These powders were dispersed into 0.4 mol/l sol–gel solution with power/solution molar composition maintained at 1:2 to form the precursor for the sol–gel based ceramic–ceramic 0-3 composite method.

PVP was proved to be effective in retarding condensation and promoting structural relaxation in film subjected to heat treatment [21]. In PVP-assisted sol–gel method, PVP powders were first dissolved in acetic acid and then added to the \(\text{Pb}(\text{CH}_3\text{COO})_2\)-\(\text{CH}_3\text{COOH}\) solution. The molar composition of \(\text{Pb}/\text{PVP}\) was
maintained at 1:0.5. The final stages of the solution preparation process were as described for the conventional method [24].

These resulting precursors were spin-coated on Pt/Ti/SiO$_2$/Si substrate, heated to 350$^\circ$C for 1 h and 600$^\circ$C for 20 min after preparation of each layer and finally annealed at 650$^\circ$C for 4 h in N$_2$ atmosphere.

In our ESD system, 0.4 mol/l PZT solution was used as precursor. When electrically charged beyond a critical level at the outlet of the capillary, the surface of the solution became unstable and electrostatic spray was formed [27]. Accelerated by a high-voltage electric field, the charged droplets were deposited at high speed on the substrate then the film was got. The experimental set-up and annealing process have been described in detail elsewhere [23].

To investigate the crystallization of the as-deposited PZT film, X-ray diffraction (XRD) measurements (MXP18AHF, Mac Science) were carried out. The microstructures of the film were observed using optical microscope (BX60F5, Olympus) and atomic force microscope (AFM) (Nano III, Digital Instruments). The thickness of the films was measured by surface profilometer (alpha step 500, Ten-cor). A Sawyer–Tower circuit [28] was used to measure the $P–E$ hysteresis loop of the PZT film.

3. RESULTS AND DISCUSSION

3.1. Sol–gel-based ceramic–ceramic 0-3 composite

In the sol–gel-based ceramic–ceramic 0-3 composite method, the sol–gel combustion derived cake-like crystalloid PZT powders were first grinded in a mortar and then filtered by a funnel before dispersing into the precursor solution. Ultrafine PZT powders with yellowish color can be achieved and the XRD pattern is shown in Fig. 1. It is clear that the powders are well crystallized and only the pervoskite

![Figure 1. XRD pattern of the PZT powders.](image-url)
phase can be observed in the pattern. Calculated from the half-width of the diffraction peak, the average diameter of the powder was less than 300 nm.

Using this technique, we successfully prepared a 10-µm-thick PZT film and Fig. 2 shows the film’s XRD pattern. Also, only the pervoskite phase appears in the pattern. For application in MEMS, pervoskite (100) orientation is preferred to achieve excellent piezoelectric properties. However, it was found in Fig. 2 that the film exhibits pervoskite (110) orientation, which is similar to the XRD pattern of the PZT powder. We believe that the randomly oriented PZT powders affected the orientation of the film.

The thickness of the 11-layer PZT film was 10 µm and no cracks were found in the optical micrograph shown in Fig. 3. That means more than 0.9-µm-thick PZT film can be achieved in an individual layer. It extremely exceeds the critical thickness of the film prepared by conventional sol–gel method, which is 120 nm, and is favorable

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**Figure 2.** XRD pattern of the PZT film prepared by the sol–gel-based ceramic–ceramic 0-3 composite method.

**Figure 3.** Optical micrograph of the PZT film prepared by the sol–gel-based ceramic–ceramic 0-3 composite method.
for thick PZT film fabrication. According to the measured hysteresis loop shown in Fig. 4, the film exhibits excellent remanent polarization and coercive fields of 41.0 $\mu$C/cm$^2$ and 53.3 kV/cm, respectively. The relative dielectric constant of the film, as high as 1050, was measured. It is comparable to that of the film prepared by conventional sol–gel method [7].

In this technique, the percentage of the gel in the film is decreased and less shrinkage occurs when the film processed, which results in higher critical thickness. It is an effective technique for crack-free PZT film fabrication with both excellent electric properties and thickness of more than 10 $\mu$m. However, we found that the surface roughness $R_a$ of the 10-$\mu$m-thick films was 0.6 $\mu$m and augmented with increasing powder concentration. Furthermore, strongly (100) orientated PZT thick film is difficult to achieve, since the randomly oriented PZT powders will affect the film’s crystallization and growth-behavior. For application in MEMS, many researches should be conducted on this PZT film deposition technique to improve the film’s surface roughness and achieve preferred film orientation.

3.2. PVP-assisted sol–gel method

PVP can be decomposed completely at 350°C, which quite below the crystallization temperature of PZT film. Figure 5 shows the XRD pattern of 2.1-$\mu$m-thick crack-free PZT film prepared by the PVP-assisted sol–gel method. Under the induction of the (111) oriented Pt bottom electrode, which has a similar lattice constant as the PZT (100), this film exhibits only pervoskite phase and preferred (100) orientation. Using PVP powders as additive to promote structural relaxation during heat treatment, the critical thickness of individual layer can be increased to more than 0.5 $\mu$m. It was effective to increase the critical thickness of the PZT film and has little effect on nucleation and crystallization of films.

Many evidences have proved that the using of buffer layer influences the preferred orientation, as well as surface morphology of the film [29, 30]. To increase the

Figure 4. $P–E$ hysteresis loop of the PZT film prepared by the sol–gel-based ceramic–ceramic 0–3 composite method (measured at frequency of 1 kHz).
Figure 5. XRD pattern of the PZT film prepared by the PVP-assisted sol–gel method.

preferred (100) orientation, 100-nm-thick strongly (100) oriented sol–gel-derived PZT film was used as buffer layer between as-deposited PZT film and the substrate. The XRD pattern shown in Fig. 6 reveals that the obtained film strongly oriented in pervoskite (100). The use of sol–gel-derived PZT film as buffer layer greatly affects the as-deposited PZT film’s nucleation and growth behavior and notably enhances the pervoskite (100) orientation.

Figure 7 shows the AFM image of the PZT thick film prepared by the PVP-assisted sol–gel method. It exhibits uniform grain size distribution of about 50 nm. Due to the decomposition of the PVP in the film, the microstructure of the film is not as dense as that of the film prepared by the conventional sol–gel method. The relative dielectric constant of the film is 600.

In the PVP-assisted sol–gel method, PVP powders are used as chelating agents, which retard the condensation reaction, promote structural relaxation and reduce the inner-stress of the film. It significantly enhances the critical thickness of sol–gel-
derived PZT films. Although the electric properties of the film still make it difficult to satisfy the requirements of microsensors and microactuators, this method is still a promising technique for PZT thick film fabrication with preferred orientation.

3.3. Electrostatic spray deposition

The sol–gel-based ceramic–ceramic 0-3 composite technique and the PVP-assisted sol–gel technique are capable of fabricating PZT film with desired film thickness and acceptable film properties. However, the spin-coating process is relatively complicated and time-consuming. Based on this standpoint, we introduced a novel deposition technique, named ‘electrostatic spray deposition (ESD)’, to PZT thick film preparation. In our ESD system, the steadiest spray mode, named ‘cone-jet’ mode, can be achieved at applied electric potential of 4500 V and solution flow rate of 0.6 ml/h for the 0.4 mol/l PZT precursor solution (Fig. 8). It is the precondition for large area and uniform film deposition.

Figure 9a shows the XRD pattern of 1-µm-thick PZT film deposited at a substrate temperature of 25°C. Only pervoskite phase appears in the pattern and no preferred orientation was found. In this method, strongly (100) oriented sol–gel derived PZT film was also used as buffer layer. The XRD patterns are shown in Fig. 9b and 9c. Similarly, affected by the orientation of the buffer layer, the ESD-deposited PZT film also exhibits preferred strong pervoskite (100) orientation.

High substrate temperature during deposition results in quick evaporation of solvent in real time, which is advantageous for relaxing inner-stress and favorable for thicker PZT film deposition. The XRD patterns of the buffer layer and sol–gel-buffered ESD PZT film deposited at 100°C are shown in Fig. 10. It reveals that preferred (100) orientation could also be achieved at high substrate temperature.

The microstructures of the ESD-PZT film deposited at substrate temperatures of 25°C and 100°C were observed by AFM (Fig. 11). Obviously, the film deposited at different substrate temperature exhibits similar crystallite size distribution, which is
uniform in sizes of 150 nm to 200 nm and similar to that of the film deposited by jet molding system  [18].

In the ESD system, more than 0.5-μm-thick crack-free PZT film can be achieved in an individual layer, which decreases the influence of Pt bottom electrode and buffer layer on nucleation and orientation of the ESD-deposited PZT film. To achieve preferred strong pervoskite (100) orientation, as well as to achieve denser microstructure, sol–gel PZT was used as multi-seeding layer [31] between each layer of ESD-deposited PZT film. The $P–E$ hysteresis loop of a 2-μm-thick PZT film deposited at 25°C using seeding layers is shown in Fig. 12. The film exhibits acceptable remanent polarization and coercive fields of 12.5 $\mu C/cm^2$ and 32 kV/cm, respectively. The relative dielectric constant of the film, 960, was measured, which is comparable with that of the film prepared by the sol–gel-based ceramic–ceramic 0-3 composite method.
Figure 10. Comparison of XRD patterns between (a) sol–gel PZT buffer layer and (b) ESD PZT film deposited at 100°C with the buffer layer.

Figure 11. AFM images of ESD-deposited PZT film deposited at substrate temperature of (a) 25°C and (b) 100°C.

Figure 12. $P–E$ hysteresis loop of ESD-deposited PZT film measured at a frequency of 1 kHz.
The target of our research is to find an effective fabrication technique for PZT film preparation with both desired film thickness and excellent film properties. In this paper, PZT films with thickness ranges from 2 \( \mu \text{m} \) to 10 \( \mu \text{m} \) were successfully prepared by three modified sol–gel techniques. The properties of these films are acceptable for application in MEMS. As a new technique, ESD offers attractive advantages over other two methods of easy control of substrate temperature during deposition: easy control of film composition, high film growth rate and is suitable for industrial production. The modification of the spray cloud to achieve strongly pervoskite (100) oriented PZT thick film with denser microstructure and the simplification of heat treatment process will further promote the application of this method in MEMS technology. Further investigation of these modified sol–gel techniques is also in progress.

4. CONCLUSIONS

PZT films with both satisfying film properties and thickness of more than 2 \( \mu \text{m} \) have been prepared successfully by the sol–gel-based ceramic–ceramic 0-3 composite method, PVP-assisted sol–gel method and ESD on Pt/Ti/SiO\(_2\)/Si substrate. The critical thickness of the film was sufficiently increased by using PZT powders and PVP as additives and by electrostatic spray technique. The electric properties of the as-deposited PZT thick films are acceptable, which made these techniques possible for application in micro electromechanical system technology.

REFERENCES


\textbf{ABOUT THE AUTHORS}

\begin{figure}[h]
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\includegraphics[width=0.7\textwidth]{JianLu}
\caption{Jian Lu} received his bachelor’s degree in 2000 from University of Science and Technology of China (USTC). He is now a PhD candidate at USTC. His research interests include thick PZT film preparation, piezoelectric properties of PZT films measurements and PZT-film-based micro-devices.
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\includegraphics[width=0.7\textwidth]{JiaruChu}
\caption{Jiaru Chu} received his PhD degree in 1997 from USTC. In 1998–2000, he worked as an NEDO industrial technology researcher in the Mechanical Engineering Laboratory, AIST/MITI (Japan). He is currently a Professor and Chairman of the Department of Precision Machinery and Precision Instrumentation (USTC). His research interests include integrated microsensors and microactuators, novel fabrication techniques for micro- and nano-devices, and packaging techniques for micro-nano systems.
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\includegraphics[width=0.7\textwidth]{YanYang}
\caption{Yan Yang} received her bachelor’s degree in 2002 from University of Science and Technology of China (USTC). She is now a master student of Hong Kong Polytechnic University. Her research interest is thick PZT film preparation for application in MEMS technology.
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